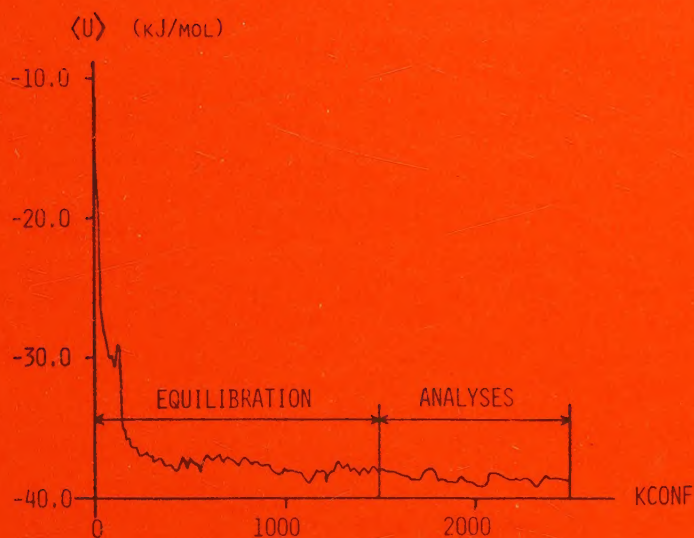


ON THE INTERPRETATION OF NMR SPECTRA OF QUADRUPOLEAR NUCLEI - QUANTUM CHEMICAL AND STATISTICAL MECHANICAL CALCULATIONS

Sven Engström



Lund 1980

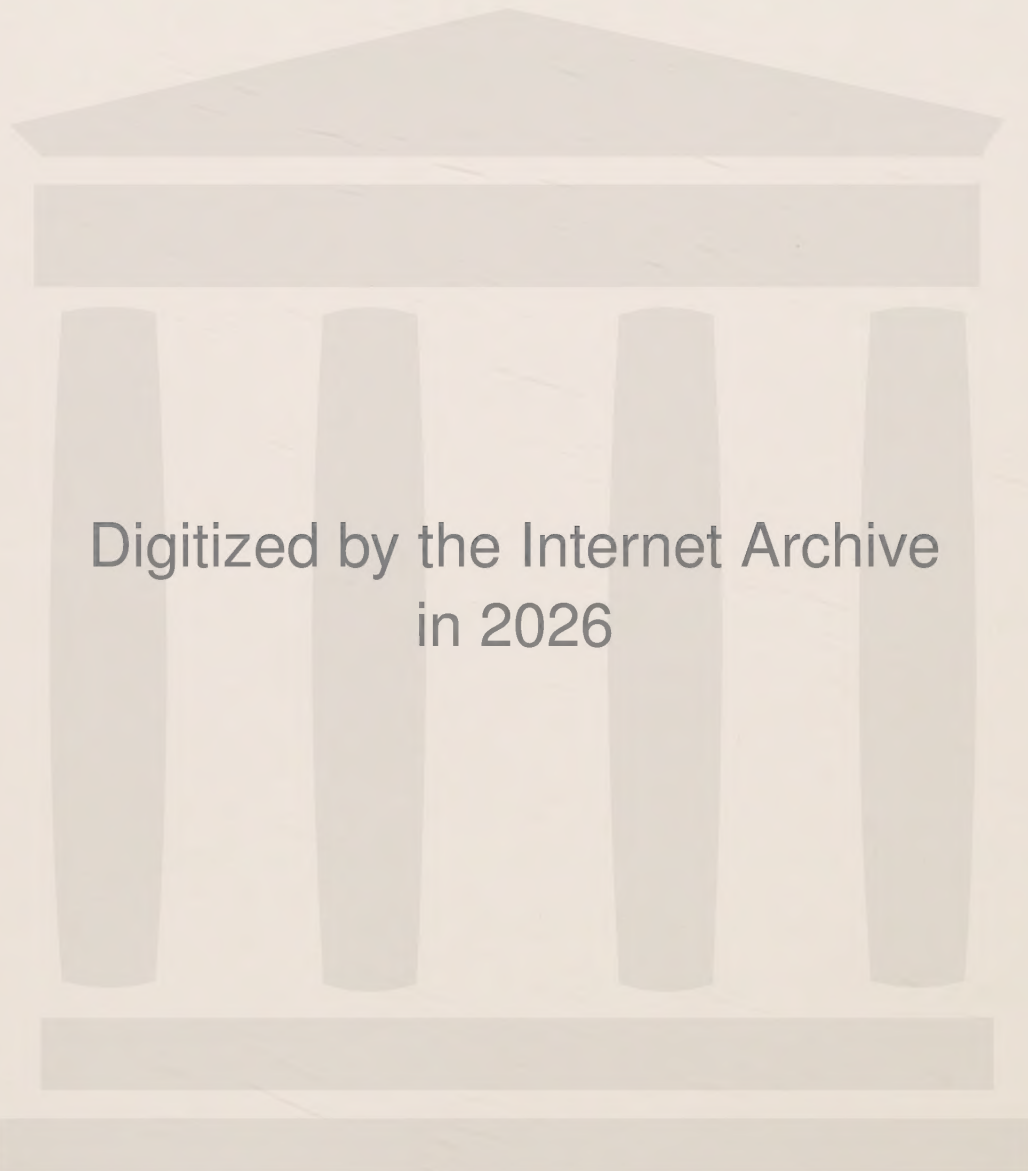
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ON THE INTERPRETATION OF NMR SPECTRA OF QUADRUPOLEAR NUCLEI -
QUANTUM CHEMICAL AND STATISTICAL MECHANICAL CALCULATIONS

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Title and subtitle ON THE INTERPRETATION OF NMR SPECTRA OF QUADRUPOLEAR NUCLEI -
QUANTUM CHEMICAL AND STATISTICAL MECHANICAL CALCULATIONS

Abstract The effects of perturbing electric fields and field gradients on the nuclear quadrupole coupling in molecules were investigated using an ab initio MO-SCF method. The theories for the first-order effects, due to the electronic and nuclear distortions, were developed. It was found that the electronic contribution, the Sternheimer shielding, is more complex for molecules than for atomic systems, since the shielding is orientation dependent, and electric fields can induce contributions as well. The nuclear deformation gives contributions of the same order of magnitude as the electronic distortion.

The electric field gradient fluctuation at a Li^+ nucleus in dilute aqueous solution was calculated via Monte Carlo simulations, using quantum chemically determined interaction potentials. The fluctuation was found to arise from lateral distortions of the water molecules in the first hydration shell. The correlation time associated with the fluctuation was 1 picosecond. For Na^+ and Cl^- the corresponding times were found to be 0.4 and 0.6 picoseconds respectively.

The Poisson-Boltzmann equation was solved for the case of two parallel charged plates with an intervening solution containing only counterions. The solution to the PB equation shows several interesting properties with respect to the ion distribution, which in the case of rod-shaped polyelectrolytes have been termed "ion condensation". The competitive "binding" of alkali counterions in a lamellar phase was taken into account by an extended form of the PB equation in three different ways.

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3/12 1980

TABLE OF CONTENTS

1. LIST OF PAPERS	1
2. INTRODUCTION	2
3. BASIC NMR OF QUADRUPOLEAR NUCLEI	4
3.1 The Quadrupole Coupling	4
3.2 The Electric Field Gradient and Its Symmetry Properties	4
4. QUANTUM CHEMICAL CALCULATIONS	6
4.1 The Hartree-Fock Method	6
4.2 Basis Sets for Calculations of Molecular Properties	7
4.3 Nuclear Electric Field Gradients and Molecular Shieldings	10
4.4 Quantum Chemical Calculations as a Basis for Monte Carlo Simulations	13
5. STATISTICAL MECHANICAL CALCULATIONS 1	15
5.1 Quadrupolar Ion Relaxation in Dilute Aqueous Solution	15
5.2 The Monte Carlo Simulation Technique	16
5.3 The Electric Field Gradient Fluctuation	17
5.4 Hydration Numbers and Geometries of the First Shell for Li^+	18
5.5 Recent Calculations	20
5.5.1 $\langle V_{zz}^2 \rangle$ and τ_{eff} for Na^+ and Cl^-	20
5.5.2 Three-Body Corrections to the Energy	20
5.6 Future Projects	22
6. STATISTICAL MECHANICAL CALCULATIONS 2	24
6.1 Quadrupolar Splittings in Lamellar Liquid Crystals	24
6.2 The Poisson-Boltzmann Equation	25
6.3 Ion Condensation in Lamellar Liquid Crystals	26
6.4 Counterion Specificity in Lamellar Liquid Crystals	27
6.5 Future Projects	31
7. ACKNOWLEDGEMENTS	33
8. REFERENCES	34

1. LIST OF PAPERS

The present thesis consists of this summary and the following papers (in the summary denoted by their Roman numerals):

I STERNHEIMER SHIELDING IN MOLECULES

S. Engström, H. Wennerström, B. Jönsson and G. Karlström,
Mol. Phys., 34, 813 (1977).

II NUCLEAR QUADRUPOLE COUPLING AND MOLECULAR DEFORMATIONS

S. Engström and H. Wennerström,
Mol. Phys., 36, 773 (1978).

III MONTE CARLO SIMULATIONS OF THE ELECTRIC FIELD GRADIENT FLUCTUATION AT THE NUCLEUS OF A LITHIUM ION IN DILUTE AQUEOUS SOLUTION

S. Engström and B. Jönsson,
submitted to Mol. Phys.

IV ION CONDENSATION ON PLANAR SURFACES. A SOLUTION OF THE POISSON- BOLTZMANN EQUATION FOR TWO PARALLEL CHARGED PLATES

S. Engström and H. Wennerström,
J. Phys. Chem., 82, 2711 (1978).

V ALKALI COUNTERION BINDING SPECIFICITY IN LAMELLAR LIQUID CRYSTALS

O. Söderman, S. Engström and H. Wennerström,
J. Colloid Interface Sci., in press.

2. INTRODUCTION

All calculations performed in this thesis are, in one way or another, relevant for the interpretation of nuclear magnetic resonance (NMR) spectra of atomic nuclei with electric quadrupole moments. Many elements in the periodic table have at least one isotope with that property, and they are being shown an ever increasing interest in NMR spectroscopy, not least in studies of biological systems (1,2).

The interaction between the quadrupole moment and its environment, the so-called quadrupole coupling, occurs through the electric field gradient produced by the surrounding charge distribution. Besides the Zeeman interaction, the quadrupole coupling dominates the NMR spectroscopic behaviour of most quadrupolar nuclei. Due to certain properties of the field gradient, the quadrupolar interaction is heavily dependent on the symmetry of the surroundings. A correct understanding of NMR data from samples containing quadrupolar nuclei will therefore provide both structural and dynamical information about the systems.

The theoretical calculations to be presented in this summary concern three different aspects of quadrupolar NMR. In papers I and II, attention is focused on the induced contributions to the nuclear electric field gradient in a molecule, when the latter is perturbed by external electric fields and field gradients, as in condensed media. These calculations were performed with a quantum chemical method, the Hartree-Fock method, and the results obtained are summarized in section 4.

In paper III, intermolecular contributions to the field gradient are included as well, in an attempt to calculate the field gradient, or rather its fluctuation, at a Li^+ nucleus surrounded by up to 150 rigid H_2O molecules. These calculations were accomplished by using a statistical mechanical method, the Monte Carlo simulation technique. The results in paper III, which are relevant for the interpretation of data from quadrupolar relaxation measurements, are summarized in

section 5, where some recent calculations on systems containing Na^+ and Cl^- are also presented (3).

Papers IV and V, summarized in section 6, do not treat the electric field gradient explicitly, but concentrate on the distribution of quadrupolar ions in a lamellar liquid crystalline phase. This system is mimicked by a simple electrostatic continuum model. The properties of the solution to the Poisson-Boltzmann equation, applied to the model, are seen to confirm experimental NMR findings from lamellar systems. In paper V, competitive counterion binding in a lamellar phase is studied experimentally, and taken into account theoretically in three different ways, by an extended form of the Poisson-Boltzmann equation.

Several different theoretical frameworks are involved in this thesis, but it does not seem necessary to present any of them in detail. Instead the reader is referred to the references given in the text for more comprehensive treatments. Furthermore, in some cases a reference is made to an equation, a table or a figure in one of the papers I-V, with for example the notation "Eq. (III:2)", thus with the meaning Eq. (2) in paper III.

Finally, in a summary like this one is supposed to review the essential results and conclusions from previous work. This has hopefully been done, but, in addition, I have taken the opportunity to sketch a few projects, in line with the present calculations, which seem feasible to carry out within the near future.

3. BASIC NMR OF QUADRUPOLEAR NUCLEI (4)

3.1 The Quadrupole Coupling

An atomic nucleus with a spin quantum number $I > 1/2$ possesses an electric quadrupole moment, eQ , due to non-spherical distribution of nuclear charges. The quadrupole moment interacts with an electric field gradient at the nuclear site, arising from all charges in the surroundings. Formally, the quadrupole coupling can be introduced into the spin Hamiltonian as an additional term,

$$\hat{H} = -\nu_L \hat{I}_z + \frac{eQ}{2I(2I-1)\hbar} \cdot \sum_{M=-2}^2 (-1)^M V_{-M}^2(t) \hat{A}_M^2 \quad (\text{in Hz}) \quad (1)$$

In Eq. (1) ν_L is the Larmor frequency, $V_{-M}^2(t)$ is a component of the electric field gradient tensor, and $\hat{A}_M^2$ a tensor component of a nuclear spin operator.

The quadrupole coupling determines the NMR spectra in at least two respects. Since the field gradient varies with time, due to the molecular motions, the fluctuating quadrupole coupling causes relaxation of the nuclear spins, when they have been perturbed from their equilibrium distribution. Furthermore, if the time-variation is slow, compared to the inverse of the quadrupole coupling, a splitting of the ordinary Larmor signal results. Paper III deals with the first case, and papers IV and V with the second.

3.2 The Electric Field Gradient and Its Symmetry Properties

The electric field gradient is a second-rank tensor with the irreducible components

$$\begin{aligned} V_0^2 &= \frac{\sqrt{6}}{2} V_{zz} \quad , \quad V_{\pm 1}^2 = \mp (V_{xz} \pm iV_{yz}) \quad , \\ V_{\pm 2}^2 &= \frac{1}{2} (V_{xx} - V_{yy} \pm 2iV_{xy}) \end{aligned} \quad (2)$$

where.

$$V_{\alpha\beta} = \frac{\partial^2 V}{\partial \alpha \partial \beta} \quad (\alpha, \beta = x, y, z) \quad (3)$$

In Eq. (3) V is the electric potential, and the derivatives are to be taken at the nucleus of interest. The field gradient tensor is normally evaluated in a coordinate system fixed at the quadrupolar nuclei, in which all off-diagonal components of the tensor are zero, i.e. a principal axes system. In that coordinate system, the so-called molecular system (M), the two independent components are chosen to be

$$eq \equiv V_{zz}^M \quad (4)$$

and the asymmetry parameter

$$\eta \equiv \frac{V_{xx}^M - V_{yy}^M}{V_{zz}^M} \quad (5)$$

where the principal components in Eqs. (4) and (5) are ordered according to $|V_{zz}^M| \geq |V_{yy}^M| \geq |V_{xx}^M|$. The quadrupole coupling constant can be defined as

$$\chi \equiv e^2 Qq/h \quad (\text{in Hz}) \quad (6)$$

If the nucleus under consideration is situated at the intersection of two at least three-fold rotational symmetry axes, e.g. tetrahedral or octahedral symmetry, the field gradient tensor vanishes. If there is only one such axis, e.g. linear or pyramidal symmetry, η is zero. The importance of these symmetry properties will be exemplified in the following sections.

4. QUANTUM CHEMICAL CALCULATIONS

4.1 The Hartree-Fock Method (5)

The electric field gradient at a particular point in a molecular (or atomic) system with fixed nuclear positions (i.e. Born-Oppenheimer approximation), is represented by an expectation value of a suitable operator (Eq. (7)).

$$\langle V_{\alpha\beta} \rangle = \langle \Psi | -e \sum_i \frac{3\alpha_i\beta_i - r_i^2 \delta_{\alpha\beta}}{r_i^5} | \Psi \rangle / \langle \Psi | \Psi \rangle + V_{\alpha\beta}^n \quad (\alpha, \beta = x, y, z) \quad (7)$$

In Eq. (7) Ψ is the total electronic wave function, r_i the distance between electron i and the point of interest, δ is the Kroenecker delta, and $V_{\alpha\beta}^n$ is the contribution from the fixed nuclei in the molecule. Given the wave function Ψ , it is a relatively simple matter to calculate the field gradient, since it is a one-electron property.

All quantum chemical calculations in this thesis were performed within the so-called Hartree-Fock (HF) approximation, using the computer program system MOLECULE (6). The HF method is an ab initio method, indicating that no empirical data except for some fundamental constants (m_e , e and h) are included in the calculations. One serious approximation made at the HF level is the partial neglect of electron correlation. Thus, in the HF method, one electron interacts with the average potential created by the others in the system. In order to improve the description, one has to go beyond the HF level, and use some configuration interaction (CI) technique. However, CI calculations are very expensive at present, since they require a large amount of computer time.

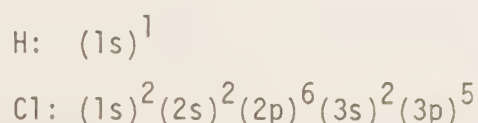
The molecular orbitals (MO's) in this particular HF variant are expanded as linear combinations of atomic orbitals (LCAO's). The AO's are in turn expanded in sets of Gaussian functions

$$\phi = \sum_i C_i x^l y^m z^n e^{-\xi_i r^2} \quad (8)$$

normally centered at the nuclei in the molecule. In Eq. (8) C_i is an expansion coefficient, l , m and n are positive integers determining the symmetry of the function, and ξ_i an orbital exponent. The appropriate choice of Gaussian atomic basis sets for calculations of molecular properties has been discussed by Dunning and Hay (7), and Ahlrichs and Taylor (8). A rule of thumb is that the larger the basis sets, the better the agreement with experiment, but at the cost of computational effort.

4.2 Basis Sets for Calculations of Molecular Properties

In order to illustrate the importance of the choice of atomic basis sets, we shall calculate some molecular properties of HCl, with basis sets of different quality. The electronic configuration of the isolated H and Cl atoms are, adopting the shell model,



A reasonable choice of basis functions would be one set of Gaussian s-functions ($l=m=n=0$ in Eq. (8)) on H and three different sets of s-functions and two different sets of p-functions ($l+m+n=1$ in Eq. (8)) on Cl. This choice is termed a "single zeta" (SZ) or "minimal basis" (MB) set, since each shell is represented by one set of Gaussian functions. A "double zeta" (DZ) basis set for each atom is obtained if two Gaussian sets describe each atomic shell.

The basis sets reported in the literature are usually optimized (i.e. the expansion coefficients, C_i 's, and the orbital exponents, ξ_i 's, in Eq. (8)) in order to obtain as low energy as possible for the isolated atoms. However, when the atoms are used to form a molecule, the atomic orbitals become distorted, especially in the outer shells. In order to allow for this distortion, one usually adds so-called polarization (P) functions to the atomic basis sets; in this example, p-functions on H, and d-functions ($l+m+n=2$ in Eq. (8)) on Cl. The effect of

the P functions are to substantially lower the total energy of the molecule. Basis sets of DZ+P quality were used in all of the calculations reported in (I) and (II). In paper III larger basis sets were used, hereafter referred to as "extended" (EXT) basis sets.

Unfortunately, for the calculations in the papers I-III, the present DZ+P and EXT basis sets are not sufficient to account for more than a part of the rearrangement of the electronic clouds when the molecules are subjected to external fields (9,10). For example, the dipole polarizability, α , is underestimated with these basis sets. Inclusion of "diffuse" (D) functions, with small orbital exponents, ξ_j 's, improves the results considerably. The diffuse functions make the wave function flexible enough to respond to external perturbations. In the case of HCl one adds diffuse s- and p-functions on H, and diffuse s-, p- and d-functions on Cl.

Some results from HF calculations on the HCl molecules at its equilibrium geometry (1.275 Å) are shown in Table 1. The EXT basis set used

Table 1. Properties of HCl from HF calculations.

Basis set	Energy (a.u.)	μ (D)	$V_{zz}(\text{Cl})$ (a.u.)	F_{00} (Å ⁻¹)	G_{00}
DZ	-460.05023	1.93	3.72	-12	48
DZ+P	-460.07922	1.43	3.48	-19	39
EXT+D	-460.10209	1.24	3.64	-9	55
best HF §	-460.1103				
exp.	-462.184	1.08	3.66		

§ P.E. Cade and W.M. Huo, J.Chem.Phys., 47, 649 (1976).

in this case is not the same as in (III), but still larger ("triple zeta"). The energy obtained with the EXT+D basis set is not far from the best possible within the HF approximation, the so-called "Hartree-Fock limit". In order to do better, one has to use some CI technique.

The dipole moment, μ , is seen to change drastically with the size of the basis set used (Table 1). The electric field gradient at the chlorine nucleus, represented by its V_{zz} -component in Table 1, shows no clear trend when the basis set is made larger. However, the DZ value should not be taken too seriously, since the field gradient is largely an effect of the H-Cl bond, which is badly described with a DZ basis set.

In Table 2 the contributions to V_{zz} from each of the 9 occupied MO's in HCl are listed (EXT+D basis set), together with corresponding contributions in Cl^- . The dominant atomic orbitals

Table 2. MO contributions to $V_{zz}(\text{Cl})$ in HCl and Cl^- obtained with the EXT+D basis set.

MO	Dominating AO's	$V_{zz}(\text{Cl})(\text{a.u.})$	
		HCl	Cl^-
1	1s(Cl)	0.00	0.00
2	2s(Cl)	0.00	0.00
3	2p _z (Cl)	-160.18	-160.54
4	2p _x (Cl)	80.34	80.27
5	2p _y (Cl)	80.34	80.27
6	3s(Cl)	-0.22	0.00
7	1s(H)+3p _z (Cl)	-7.06	-9.22
8	3p _x (Cl)	5.14	4.61
9	3p _y (Cl)	5.14	4.61

Total electronic contribution		3.50	0.00
Nuclear contribution		0.14	0.00

Total		3.64	0.00

in each MO are also indicated in Table 2. Although the contributions from the 2p orbitals on chlorine are enormous, they largely cancel when summed

up for HCl. This is not the case for the 3p orbitals, since one of them, $3p_z$ in this case, is involved in a bond with the 1s orbital on hydrogen. For the Cl^- ion, the spherical symmetry makes the field gradient vanish, but Table 2 shows that the MO contributions are about the same as for HCl. The properties " F_{00} " and " G_{00} " (Table 2) will be defined and discussed in the following subsection.

To summarize, the basis sets used in (I-III) are, although fairly large, not capable of fully accounting for electronic polarization.

4.3 Nuclear Electric Field Gradients and Molecular Shieldings

If a molecule is brought from the gas phase to a condensed phase, the molecular shape will be altered, due to the stronger interactions with the surroundings in the latter case. For example, the dipole moment will change, and the first-order correction is the induced contribution due to the external electric field, $\vec{E}$,

$$\langle \vec{\mu} \rangle = \langle \vec{\mu} \rangle_0 + \tilde{\alpha} \cdot \vec{E} \quad (9)$$

where $\tilde{\alpha}$ is the dipole polarizability tensor. An expression similar to Eq. (9) can be written for the electric field gradient at any of the nuclei in the molecule (using spherical tensor notation for convenience):

$$\begin{aligned} \langle V_M^2(\text{nuc}) \rangle &= \langle V_M^2(\text{nuc}) \rangle_0 + \\ &+ \sum_{M'} (D_{MM'} + F_{MM'}) \cdot V_{M'}^1(\text{ext}) + \sum_{M'} (\delta_{MM'} + G_{MM'}) \cdot V_{M'}^2(\text{ext}) \end{aligned} \quad (10)$$

The first term on the right-hand side of Eq. (10) is the nuclear field gradient for the isolated molecule. The parameters $D_{MM'}$ and $F_{MM'}$ refer to the induced contributions, due to the external electric field, $V_{M'}^1(\text{ext})$ (cf. $\tilde{\alpha}$). The D-factors take the distortion of the nuclear positions into

account, and the F-factors the distortion of the electronic cloud of the molecule. The coupling between these two effects is neglected. The parameter $G_{MM'}$ corresponds to $F_{MM'}$, but it refers to the electronic polarization due to the external electric field gradient, $V_{M'}^2(\text{ext})$. The Kroenecker delta is included to take the contribution from the external field gradient itself into account. Eq. (10) represents a first-order approximation, and one should not expect it to be valid when the external fields become very strong, since higher-order effects will then be important.

For atomic systems Eq. (10) reduces, by symmetry, to

$$\langle V_0^2(\text{nuc}) \rangle = (1+G_{00})V_0^2(\text{ext}) \equiv (1+\gamma_\infty)V_0^2(\text{ext}) \quad (11)$$

where G_{00} has been replaced by γ_∞ , better known as the Sternheimer (anti)shielding factor. This factor has been theoretically determined, starting with the work by Sternheimer (11) in the early 50's, for a number of atomic systems (12,13). γ_∞ has been shown to range between -0.3 - +600, depending on the atomic system studied, and is therefore important in determining the magnitude of the quadrupole coupling.

In paper I; the concept of Sternheimer shielding was, for the first time, generalized to molecular systems as well, and the F- and G-factors were determined quantum mechanically for the nitrogen nucleus in HCN and NH_4^+ , and for the chlorine nucleus in HCl. In paper II the effects of distorting the nuclear positions for these molecules were considered, and the D-factors were calculated. One great difference between molecular and atomic systems, in this respect, is the lower symmetries of the former. This makes the shielding orientation dependent, and in addition, the electric field can induce a contribution to the nuclear field gradient. In principal there are 15 D-, 15 F- and 25 G-factors to be determined if symmetry is not taken into account, but these numbers can be substantially reduced if this is done.

Table 3 shows the shielding factors determined in (I) and (II), and from the results the following conclusions can be drawn:

Table 3. Calculated D-, F- and G-factors for N in HCN and NH_4^+ , and for Cl in HCl and Cl^- .

Shielding factors §	HCN	NH_4^+	HCl	Cl^-
D_{00}/F_{00}	0.19/6.2		1.3/-19	
D_{11}/F_{11}	-7.0/-2.5		- /0.09	
D_{1-1}/F_{1-1}		-i2.5/i4.3		
G_{00}	-2	4.0	39	38
G_{11}	2.8	10	20	
G_{22}	8		31	

$$\S [D] = [F] = \text{\AA}^{-1}$$

- i) the shielding factors (D, F and G) in molecular systems are of the same order of magnitude as γ_∞ in atomic systems, but the shielding is orientation dependent.
- ii) the induced effect from the electric field dominates.
- iii) the absolute magnitudes of the shielding factors are in sizeable error (about a factor of two), due to the limited basis sets used in (I) and (II). An indication of this is seen in Table 1, where F_{00} and G_{00} have been recalculated with a larger basis set, i.e. EXT+D, with the result that F_{00} is -9 and G_{00} is 55. However, the basis set effect is more dramatic for the Cl^- ion, for which G_{00} changes from 38 (DZ+P) to 77 (EXT+D). Thus, the hydrogen atom has a restraining influence on the electronic cloud in HCl.
- iv) Eq. (10) is valid for electric field strengths created by an elementary charge as close as 5 Å from the nucleus, with some exceptions.

4.4 Quantum Chemical Calculations as a Basis for Monte Carlo Simulations

A Monte Carlo simulation (section 5) of a system of interacting particles requires explicit expressions for the total energy of the system in terms of interparticle distances and orientations. For practical reasons, it is usually assumed that the total interaction energy is a sum of two-particle interactions. In paper III, the system studied consists of a lithium ion surrounded by water molecules (6, 50 and 150 respectively). The total interaction energy for this system is thus a sum of ion-water interactions and water-water interactions.

Both of the potential surfaces used in (III) are based on quantum chemical calculations. The ion-water potential was determined by fitting the interaction energies from 77 HF calculations on the $\text{Li}^+ + \text{H}_2\text{O}$ system at various geometries to an analytical expression of the form (including the fitted parameters):

$$\begin{aligned} \Delta E(\text{Li}^+ - \text{H}_2\text{O}) = & -\frac{0.627}{R_0} + 0.3135 \left(\frac{1}{R_{H1}} + \frac{1}{R_{H2}} \right) - \frac{0.598}{R_0^2} + \\ & + 0.171 \left(\frac{1}{R_{H1}^2} + \frac{1}{R_{H2}^2} \right) + \frac{53.131}{R_0^6} + 1.049 \left(\frac{1}{R_{H1}^6} + \frac{1}{R_{H2}^6} \right) - \\ & - \frac{1568.15}{R_0^{12}} - 1.869 \left(\frac{1}{R_{H1}^{12}} + \frac{1}{R_{H2}^{12}} \right) \quad (\text{in atomic units}) \end{aligned} \quad (12)$$

In Eq. (12), R_0 , R_{H1} and R_{H2} are the distances between the lithium ion and the atoms in the water molecule. The water-water potential, based on CI calculations, was taken from the work of Matsouka et al. (14).

The atomic basis sets used in the HF calculations on the $\text{Li}^+ + \text{H}_2\text{O}$ system were, as mentioned above, of the "extended" type, but lacked "diffuse" functions. This results in a calculated dipole polarizability, α , for the isolated water molecule, which is only 60% of the experimental value. One would thus expect that a non-negligible part of the polarization energy is missing in the ion-water potential. However, a part of

that energy is regained when the H_2O molecule is treated quantum mechanically together with Li^+ , since these species make use of each other's basis functions ("superposition error").

Since the electric field gradient at the lithium ion arising from the water molecules was of particular interest in (III), it was evaluated in each of the HF calculations as well. These field gradients were then fitted to a function of the form (including the fitted parameters):

$$\begin{aligned}
 V_{zz}(Li^+) = & \left(-\frac{1.421}{R_0^3} - \frac{5.217}{R_0^4} + \frac{24.446}{R_0^5} \right) \cdot S_0^2(\Theta_0) + \\
 & + \left(\frac{0.546}{R_{H1}^3} + \frac{0.211}{R_{H1}^4} + \frac{0.638}{R_{H1}^5} \right) \cdot S_0^2(\Theta_{H1}) + \\
 & + \left(\frac{0.546}{R_{H2}^3} + \frac{0.211}{R_{H2}^4} + \frac{0.638}{R_{H2}^5} \right) \cdot S_0^2(\Theta_{H2}) \quad (\text{in a.u.})
 \end{aligned} \tag{13}$$

In this expression the terms $S_0^2(\Theta_I)$ are given by

$$S_0^2(\Theta_I) = \frac{1}{2} (3 \cos^2 \Theta_I - 1) \quad (I=0, H1, H2) \tag{14}$$

In Eq. (14) Θ_I is the angle between the z-axis and the R_I -vector. The field gradients from the water molecules were assumed to be additive, which was found to be a satisfactory assumption (Table III:2).

5. STATISTICAL MECHANICAL CALCULATIONS 1

5.1 Quadrupolar Ion Relaxation in Dilute Aqueous Solution (4)

The quadrupolar relaxation rate, R , can be experimentally determined and theoretically related to a field gradient correlation function. Under "extreme narrowing" conditions the expression reads

$$R = \frac{3}{8} \frac{2I+3}{I^2(2I-1)} \left(\frac{eQ}{\hbar}\right)^2 \frac{1}{2} \int_{-\infty}^{+\infty} \langle V_{zz}(0)V_{zz}(t) \rangle dt \quad (15)$$

where $\langle \rangle$ denotes an equilibrium ensemble average. It should be noted that V_{zz} in Eq. (15) should be evaluated in the so-called laboratory coordinate system, instead of the molecular system (see section 2 in (III)).

The correlation function in Eq. (15) contains information about both the structure and dynamics of the system. In this particular case, with lithium ions in a dilute aqueous solution, the measured relaxation rate reflects the arrangement of the water molecules around the ions, and their mobility. In order to separate these effects it is convenient to define an "effective" correlation time (τ_{eff}) via

$$\tau_{\text{eff}} \langle V_{zz}^2(0) \rangle \equiv \frac{1}{2} \int_{-\infty}^{+\infty} \langle V_{zz}(0)V_{zz}(t) \rangle dt \quad (16)$$

where $\langle V_{zz}^2(0) \rangle$ is the average field gradient fluctuation (the argument of $V_{zz}(0)$ is left out from now on). τ_{eff} specifies the timescale associated with the field gradient variation.

Several models have been proposed to estimate the two quantities on the left-hand side of Eq. (16) for quadrupolar ions in aqueous solution (15-19). In (III), $\langle V_{zz}^2 \rangle$ was determined with the Monte Carlo technique for Li^+ in a model that mimicks a dilute aqueous solution of lithium ions at 300 K.

5.2 The Monte Carlo Simulation Technique (20,21)

Monte Carlo (MC) simulations of classical many-body systems have become important for several reasons. One is the ability to test physical theories (22), and another is to obtain information about intermolecular interactions in real systems, by comparing MC results with experimental data (23). A third application of the MC technique is used in paper III, where a property ($\langle V_{ZZ}^2 \rangle$), not directly measurable, is calculated.

The major purpose of the MC scheme is to produce a large number of configurations of the system under study, where each configuration is a member of an equilibrium ensemble. The configurations are chosen in accordance with their Boltzmann weights, by a sampling technique originated by Metropolis et al. (24). The total potential energy, to be included in the Boltzmann factor, is usually approximated as a sum of pair-interactions, as mentioned in section 4.

Once the MC run is over, one has hopefully a large number (M) of configurations (X_i 's) stored in the computer (or rather on a peripheral device) for further analyses. Of particular interest in (III) was to evaluate the average value, $\langle V_{ZZ}^2 \rangle$, and to investigate the distribution of water molecules around the lithium ion in detail.

An average value, say $\langle V_{ZZ}^2 \rangle$, may in the MC method be written as

$$\langle V_{ZZ}^2 \rangle = \frac{1}{M} \sum_{i=1}^M V_{ZZ}^2(X_i) \quad (17)$$

where M is the total number of equilibrium configurations, and X_i is a shorthand notation for the coordinates of all particles in the system. The system in the present case was a sphere, with a lithium ion at its center, and with the water molecules positioned around it, as sketched in Figure 1.

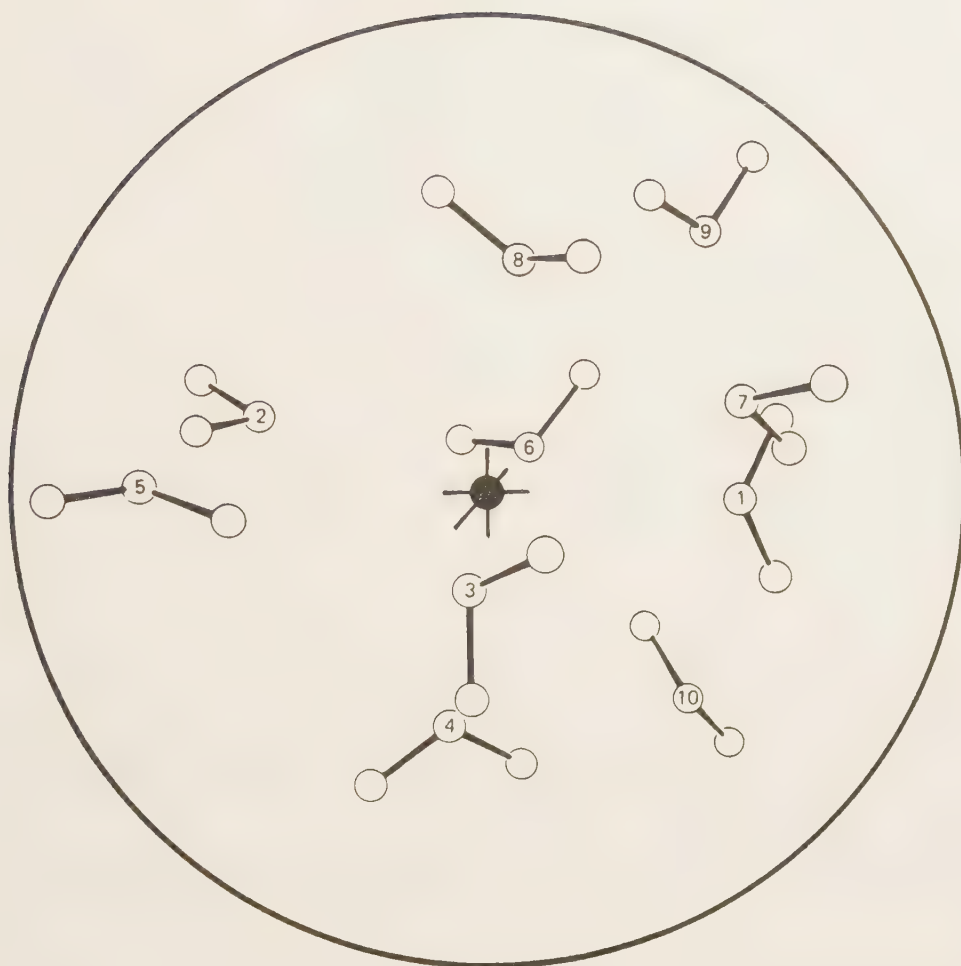


Figure 1. The Monte Carlo sphere.

5.3 The Electric Field Gradient Fluctuation

The calculations in (III) were performed under various simulation conditions, in order to investigate the sensitivity of the field gradient fluctuation to the number of H_2O 's around Li^+ , and the volume of the MC sphere. Some results from Table III:4 are listed below, in Table 4.

Table 4. Monte Carlo results for Li^+ . ρ =density of the system, $\langle V_{zz}^2 \rangle$ = the field gradient fluctuation with its rms (root mean square) deviation in parentheses. τ_{eff} =correlation time calculated with Eq. (15) using $R=0.027 \text{ s}^{-1}$ (17).

System	ρ (g/cm ³)	$\langle V_{zz}^2 \rangle \cdot 10^4$ (a.u.)§	$\tau_{\text{eff}} \cdot 10^{12}$ (s)
$\text{Li}^+ + 6\text{H}_2\text{O}$	0.91	0.15(0.03)	1.0
$\text{Li}^+ + 50\text{H}_2\text{O}$	0.91	0.14(0.05)	1.1
$\text{Li}^+ + 50\text{H}_2\text{O}$	0.37	0.14(0.04)	1.1
$\text{Li}^+ + 150\text{H}_2\text{O}$	0.91	0.11(0.05)	1.4

§ V_{zz} : 1 a.u. = $9.7175 \cdot 10^{21} \text{ Vm}^{-2}$

From the figures in Table 4 (and Table III:4) the following conclusions can be drawn:

- i) the water molecules outside the first hydration shell play a minor role for the magnitude of the fluctuation, since the results with 6, 50 and 150 H_2O 's are roughly the same.
- ii) the density in the sphere does not influence the magnitude of $\langle V_{zz}^2 \rangle$.
- iii) the values obtained for $\langle V_{zz}^2 \rangle$ seem physically reasonable, since they imply an effective correlation time, τ_{eff} , of about 1 pico-second.

5.4 Hydration Numbers and Geometries of the First Shell for Li^+

The hydration numbers that can be estimated from the present MC simulations are not directly comparable to experimental values, since the latter are obtained with finite, often high, salt concentrations. Nevertheless, comparison with experiment may serve as a test of the quality of the model. In Table 5 some experimental neutron diffraction data on LiCl in water are given (25), together with the MC data for $\text{Li}^+ + 150 \text{H}_2\text{O}$. The agreement between theory and experiment must be considered satisfactory.

Table 5. Structure data for the first hydration shell of Li^+ obtained from neutron diffraction and Monte Carlo simulations.

System	Li^+ -Oxygen distance (Å)	Li^+ -Deuterium distance (Å)	Hydration number
LiCl (3.57 molal)	1.95 ± 0.02	2.55 ± 0.02	5.5 ± 0.3
$\text{Li}^+ + 150 \text{ H}_2\text{O}$	2.02 ± 0.03	2.67 ± 0.04	5.5 ± 0.5

According to Table 5 the hydration number for Li^+ is 5.5. This value is interesting since it implies a non-cubic average arrangement of water molecules, strictly speaking, water oxygens, around the lithium ion. This symmetry, or rather lack of symmetry, will in turn result in a non-vanishing contribution to the field gradient from the first hydration shell.

In some of the theories developed to explain the quadrupolar relaxation, it is assumed that the hydration is of either tetrahedral or octahedral symmetry (16,19). The analysis in (III) of the more than 10^6 configurations generated for the $\text{Li}^+ + 150 \text{ H}_2\text{O}$ system shows that these symmetric arrangements of the water oxygens are possible (Figure III:4).

However, the magnitude of $\langle V_{zz}^2 \rangle$ varies very little over the 10^6 configurations, in spite of the fluctuating hydration number. Furthermore, MC simulations performed with the water oxygens fixed octahedrally around the Li^+ ion, allowing for the rotation of the water molecules around the oxygens only, gave about 1/10 of the total field gradient fluctuation.

Taken together, these observations indicate that the field gradient fluctuation at the lithium ion in dilute aqueous solution is mainly due to lateral distortions of the water molecules in the hydration complex, and is to a lesser extent a consequence of rotational motions of individual water molecules.

5.5 Recent Calculations (3)

5.5.1 $\langle V_{zz}^2 \rangle$ and τ_{eff} for Na^+ and Cl^-

MC simulations were recently undertaken on the systems $\text{Na}^+ + 50 \text{ H}_2\text{O}$ and $\text{Cl}^- + 50 \text{ H}_2\text{O}$. The energy and field gradient functions were of the same forms as for Li^+ (Eqs. (12-14)), also based on quantum chemical calculations. In Table 6 the most relevant results from the sodium and chloride simulations are given, together with appropriate lithium data. The effective correlations times differ slightly for the three systems, according to Table 6, but it is difficult to relate these differences to any particular motions of the water molecules in the first hydration shells.

Table 6. Monte Carlo results for Li^+ , Na^+ and Cl^- . KCONF=number of configurations in thousands. τ_{eff} is calculated with Eq. (15) using $R_{\text{Na}^+} = 16.2 \text{ s}^{-1}$ and $R_{\text{Cl}^-} = 42 \text{ s}^{-1}$ (17).

System	KCONF	ρ (g/cm ³)	$\langle V_{zz}^2 \rangle \cdot 10^4$ (a.u.)	$\tau_{\text{eff}} \cdot 10^{12}$ (s)	Hydration number
$\text{Li}^+ + 50\text{H}_2\text{O}$	1200	0.91	0.14(0.05)	1.1	5.3±0.4
$\text{Na}^+ + 50\text{H}_2\text{O}$	400	0.91	35(16)	0.4	6.0±0.2
$\text{Cl}^- + 50\text{H}_2\text{O}$	400	0.91	99(50)	0.6	5.6±0.5

5.5.2 Three-Body Corrections to the Energy

In the MC simulations presented so far in this summary, the total interaction energy of a system was approxiamted by a sum of two-particle terms. Consequently, a water-water interaction, for a given relative orientation of the water molecules, is constant, irrespective of the position of the ion. However, the electric field from the ion will polarize the water molecules, and the resulting induced dipole moments will give rise to an additional water-water interaction energy (higher-order ef-

fects are neglected). This effect is of particular importance for the water molecules in the first hydration shell.

In some recent MC simulations we have made an attempt to estimate the consequences of this type of polarization correction for the magnitude of $\langle V_{zz}^2 \rangle$ and the hydration of Li^+ . The three-body term was included in the simulations in the following way:

- i) an isotropic polarizability, α , was assigned to each water molecule, and positioned at the oxygen. Two values of α were used, one experimental ($1.4 \text{ \AA}^3$), and the other obtained from quantum chemical calculations on H_2O ($0.8 \text{ \AA}^3$). All polarizabilities of higher order, i.e. hyperpolarizabilities, were neglected. Since the latter are of importance when the electric field becomes strong, as is the case in the first hydration shell, the use of α only, must be considered as a rough approximation of the three-body effects. Furthermore, the α -values used in the present case will exaggerate the effects, since the higher-order polarizabilities give a contribution to the induced dipole moment of opposite sign to that of α .
- ii) the ion in the system was assumed to be a non-polarizable point charge. This assumption is fairly good for Li^+ (but hardly for Na^+ or Cl^-).
- iii) the induced dipole moment, $\alpha \cdot \vec{E}$, in one water molecule interacted with the total dipole moment in another. Two values of the permanent dipole moment were used as well, the experimental one (1.86 D) and the value obtained in the quantum chemical calculation on H_2O (2.21 D).

The results of these simulations are listed in Table 7. As expected, the three-body correction increases the water-water repulsion in

Table 7. Monte Carlo results for Li^+ including three-body corrections to the energy.

System	KCONF	μ/α (D/ $\text{\AA}^3$)	$\langle V_{zz}^2 \rangle \cdot 10^4$ (a.u.)	Hydration number
$\text{Li}^+ + 50\text{H}_2\text{O}$	300	2.21/0.8	0.16(0.06)	4
$\text{Li}^+ + 50\text{H}_2\text{O}$	300	1.86/1.4	0.18(0.07)	4

the first shell, which in turn results in a decreasing hydration number. For the lithium system the ion-water attractions in the first shell are sufficiently large to keep four water molecules with the oxygens tetrahedrally oriented, in the first shell. The values of $\langle V_{zz}^2 \rangle$ do not differ significantly from the case without the three-body correction, which is seen from Table 5.

The results in Table 7 should be taken as a rough estimate of the three-body effects in this kind of system. A more elaborate treatment, involving a quantum mechanically determined ion-water-water energy surface, is probably needed for more accurate results. Recently, Clementi et al. (26) reported a $\text{Li}^+ + 2\text{H}_2\text{O}$ potential, which was used in MC simulations, but they made no comments on the hydration in that paper.

5.6 Future Projects

The results in paper III and (3) have given important information about the magnitude of the field gradient fluctuation, and the detailed structures of the hydration shells for the ions studied. However, one important question remains, namely, the motion or motions responsible for the quadrupolar relaxation. This question can in principle be answered by performing Molecular Dynamics (MD) simulations on the systems discussed above.

In the MD procedure, originated by Alder and Wainwright (27), Newton's equations of motion for the molecules are solved, and one obtains accelerations, velocities and positions of the particles. The differential equations are evaluated at finite time-steps, of the order of 10^{-15} s, and the MD run is performed by generating (say) 10^4 such steps (10^{-11} s).

All of the information that can be obtained from a MC simulation, can also be obtained in a MD run. The great advantage with the MD method is that dynamical information about the system is given as well. To be specific, it is possible to evaluate the integral in Eq. (15) directly, thus determining the relaxation rate from a purely theoretical treatment. Comparison with experimental results will serve as a critical test of the

model used. Moreover, the functional form of the correlation function can be estimated, which is of great interest.

The MD method will also provide an opportunity to study the motions of the water molecules in detail. Perhaps is it possible to relate the effective correlation time, τ_{eff} , to some specific motion or motions of the water molecules.

Before performing MD simulations some refinements of the present model are necessary. One is the inclusion of three-body interactions in a more consistent way, and another is to go beyond the so-called cluster approximation. The latter can be accomplished by embedding the MC or MD sphere in a dielectric continuum, with the dielectric permittivity of water. The interaction between the water molecules in the sphere and the continuum occur via the image charges and the image dipoles that the water molecules give rise to in the continuum. This type of treatment has been discussed by Friedman (28) with respect to MC and MD simulations.

6. STATISTICAL MECHANICAL CALCULATIONS 2

6.1 Quadrupolar Splittings in Lamellar Liquid Crystals (29)

Figure 2 shows the phase diagram of the three-component system, sodium octanoate-decanol-water (at 293 K). In certain proportions these chemicals form stable and well-defined aggregates, and of special interest in the present case is the region marked "D" in Figure 2. In this region a

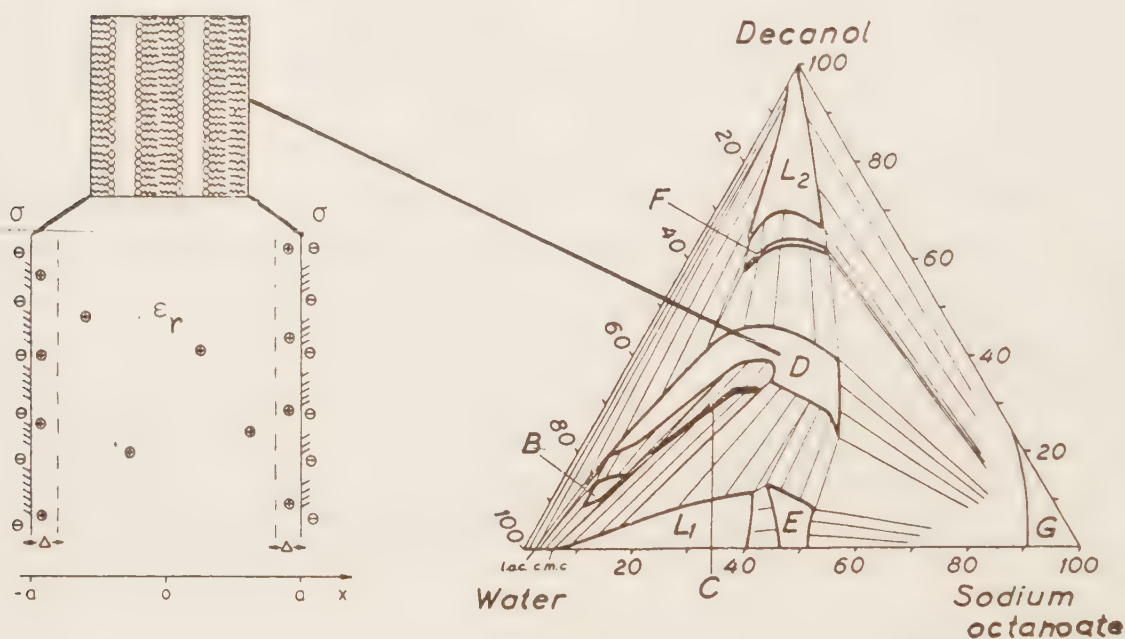


Figure 2. The phase diagram of the sodium octanoate-decanol-water system, and the lamellar phase.

so-called lamellar phase is present; its appearance is sketched in Figure 2. The lamellar phase consists of bilayers formed by the long-chain molecules, and intervening aqueous solutions, containing the counterions of the amphiphiles (sodium ions in this case). It should be noted that the phase diagram in Figure 2 is one example of many, since there is a great freedom of the choice of amphiphiles and alcohols (30).

Since the lamellar phase is anisotropic, i.e. the molecular motions are anisotropic on the time-scale given by the inverse quadrupolar in-

teractions, quadrupolar counterions in the solution region give rise to a quadrupole splitting, Δ , in the NMR spectrum. The magnitude of the splitting can, in the present case, be considered to be caused by the counterions close to the surface, i.e.

$$\Delta = |p_b \Delta_b| \quad (18)$$

where p_b is the fraction of "bound" ions, and Δ_b is the magnitude of the splitting at the "bound" site. Δ_b , in turn, is given by

$$\Delta_b = \frac{3}{4I(2I-1)} \chi_b S_b \quad (19)$$

where χ_b is the quadrupole coupling constant (Eq. (6)), and S_b the so-called order parameter. S_b contains information about the average orientation of the lamellar surface relative to the orientation of the principal axes system, in which the field gradient is determined.

In some cases the quadrupole splitting in lamellar systems is found to be roughly independent of the distances between the lamellar surfaces (e.g. 31), and the temperature (e.g. 32). The distances can be altered by changing the amount of water ("one-dimensional swelling"). The result in ref. (31) has been interpreted in terms of a constant fraction of "bound" ions, i.e. constant p_b .

In paper IV these findings have been confirmed by using a simple electrostatic continuum model to mimic the lamellar solution region. In paper V the model was extended to account for competitive counterion "binding" in the lamellar phase.

6.2 The Poisson-Boltzmann Equation

As the name indicates, the Poisson-Boltzmann (PB) equation is a fusion of the classical electrostatic Poisson equation

$$\Delta\phi = -\rho/\epsilon_r \epsilon_0 \quad (20)$$

and the Boltzmann distribution equation

$$\rho = \sum_i n_i e^{-ez_i\phi/kT} \quad (21)$$

from classical statistical mechanics. In Eqs. (20) and (21), ϕ is the electrostatic potential, ϵ_0 the dielectric permittivity of a vacuum, ϵ_r the relative permittivity, n_i a normalization constant and ez_i the charge on the i species. The sum in Eq. (21) extends over all kinds of charged species in the system (in the present case only counterions).

The PB equation has been applied to charged systems ever since the pioneering work by Gouy (33) and Chapman (34) on ion distributions outside planar surfaces. In order to apply the PB equation to the lamellar solution region, the following assumptions were made (see Figure 2):

- i) the charges on the lamellar surfaces, originating from the amphiphiles, are smeared out to a homogeneous surface charge density, σ ;
- ii) the counterions are assumed to be point charges;
- iii) the water molecules are represented by a dielectric continuum, with a permittivity constant ϵ_r ;
- iv) the lamellar surfaces are assumed to be parallel, and of infinite extension.

Due to these assumptions and the high symmetry of the model, it is possible to solve the PB equation analytically (Eqs. (IV:7-11)).

There has been some debate about the lack of consistency in the derivation of the non-linearized PB equation (e.g. 22,35). However, for this inhomogeneous system, the PB equation can be derived in a consistent way (36,37). The assumptions made in the derivation are: i) the interaction between the particles is of pure Coulomb type, and ii) the ions are uncorrelated (cf. the Hartree-Fock approximation, where the electrons are also uncorrelated to some extent).

6.3 Ion Condensation in Lamellar Liquid Crystals

The introduction of the electrostatic potential (Eq. (IV:7)) in Eq. (21) makes it possible to determine the charge distribution, once

the structural parameters of the model are fixed. These parameters have been obtained for a number of lamellar systems by X-ray diffraction studies (38). If an appropriate set of these are included in the solution to the PB equation, it reveals several interesting properties:

- i) the fraction of "bound" counterions, p_b (i.e. the fraction of ions residing within (say) 3 Å from the lamellar surface), is independent of the distance between the plates (Figure IV:4).
- ii) the counterion distribution is roughly insensitive to temperature changes, since everywhere in the equations, the temperature T is multiplied by ϵ_r , which in turn is approximately proportional to $1/T$.

Thus, the properties i) and ii) support the interpretation of the result from (31), and provide an explanation for the result in (32).

A third property which is found from the PB equation is that the fraction of "bound" ions is roughly unaffected by the addition of a simple salt to the lamellar system (39,40). This behaviour of the counterion distribution has been termed "ion condensation", for the case of rod-shaped polyelectrolytes (41,42).

The electric field gradient between the lamellar surfaces can also be obtained from the solution to the PB equation. If it is used to estimate the quadrupole splitting of sodium ions in a lamellar phase, the theoretical value is shown to be 1/10 of the experimental (40). This is not unexpected, since the field gradient at the Na^+ nucleus should be determined by local effects (e.g. hydration), which the present model cannot account for.

Finally, it should be mentioned that the PB equation has been tested by the Monte Carlo method, using the same model of the lamellar phase as in the present case (36). The result of the simulation reveals that the approximation concerning the lack of correlation between the ions is not very serious.

6.4 Counterion Specificity in Lamellar Liquid Crystals

In paper V, experimental results are reported on studies of quadru-

polar splittings of different types of alkali counterions in the same lamellar phase. These results reveal an affinity sequence $\text{Li}^+ > \text{Na}^+, \text{Cs}^+ > \text{K}^+$, which reflects the tendency of these ions to "bind" to the lamellar surface.

Since the PB equation is non-chemical, in the sense that it does not discriminate between different types of ions with the same charge, it cannot be used directly to account for ion specificity. In (V) the PB equation was extended in three different ways in order to describe the specificity. Two of the models are illustrated in Figure 3, and all models will be briefly presented below. The specificity for ion type i was defined as

$$\alpha_i = \frac{p_{ib}(X_i)}{p_{ib}(X_i=1)} \quad (22)$$

i.e. as the ratio between the fraction of "bound" i ions, when the other type of ion was present ($X_i \neq 1$), and when it was absent ($X_i = 1$). The computational techniques are described in the Appendix to paper V.

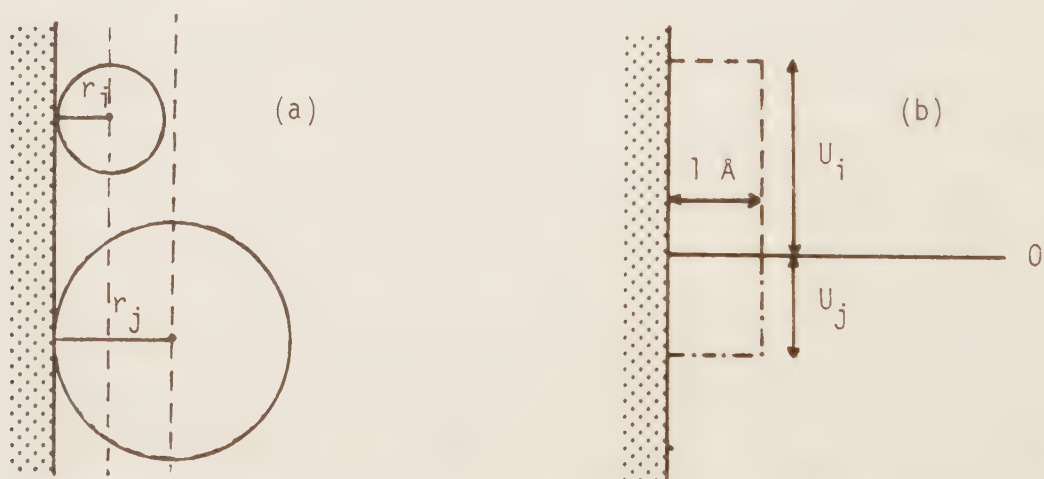


Figure 3. Ion specificity models: a) the dashed lines define the distances of closest approach, and b) the "extra" square-well potential assigned to each type of ion within $1 \text{ \AA}$ from the lamellar surface.

One way to introduce the specificity is to use the appropriate ionic radius as a measure of the distance of closest approach of an ion to the

surface (Figure 3a). In this way, small ions will always be favoured over larger ones, but it is possible to calculate the specificity with no further assumptions, using the equations from paper IV, together with appropriate boundary conditions.

In the second case, a short-range square-well potential was assigned to each type of ion, when it is near the surface (Figure 3b). These potentials can be either attractive or repulsive, and their magnitudes were determined from fits to the experimental data. The value for Li^+ was chosen to be -1.0 (in units of kT), and by this choice, the potentials for the other ions became positive, which is seen in Table 8. It is difficult to give any physico-chemical interpretation of this model, but in any case, the magnitudes of the potentials give an indication of the energies involved in the specificity.

Table 8. Ionic radii, fitted potentials, U 's, and equilibrium constants, K 's.

Counterion	Ionic radius (Å)	U/kT	K (M^{-1})
Li^+	0.60	-1.0	0.1
Na^+	0.95	1.0	0.025
K^+	1.33	1.7	0.017
Cs^+	1.69	1.0	0.025

The third model took the possibility of binding (in a stoichiometric sense) into account, and a binding constant, K , was assigned to each type of counterion. The amount of bound ions was determined from the concentration of ions in the vicinity of the lamellar surface, as given by the solution to the PB equation. Since the bound ions reduce the surface charge density, the PB equation must be re-solved until both the equilibrium equation and the PB equation are satisfied. Only strictly bound ions were assumed to give rise to the quadru-

pole splitting. As in the former model, the binding constants were obtained from fits to experimental data, and a value of 0.1 M^{-1} was chosen for Li^+ (see Table 8).

Two representative diagrams from (V) are shown in Figure 4. The abscissa shows the mole fraction of ions, and the ordinate the normalized quadrupole splitting (i.e. $\Delta_i(X_i \neq 1)/\Delta_i(X_i = 1)$) for each ion. For potassium it was not possible to monitor any splitting due to the low sensitivity of this nucleus. In the left-hand diagram of Figure 4, (Li^+, Na^+), a truly competitive behaviour is seen, since the Li^+ splitting has increased and the Na^+ splitting has decreased when the ions are mixed. The model using the ionic radii underestimates the specificity, but there is at least an order-of-magnitude agreement. The fits obtained with the other two models are reasonable.

In the right-hand diagram of Figure 4, (K^+, Cs^+), it is interesting to note that cesium seems to have a stronger affinity for the lamellar surface than potassium. Since Cs is larger than K, the first model cannot

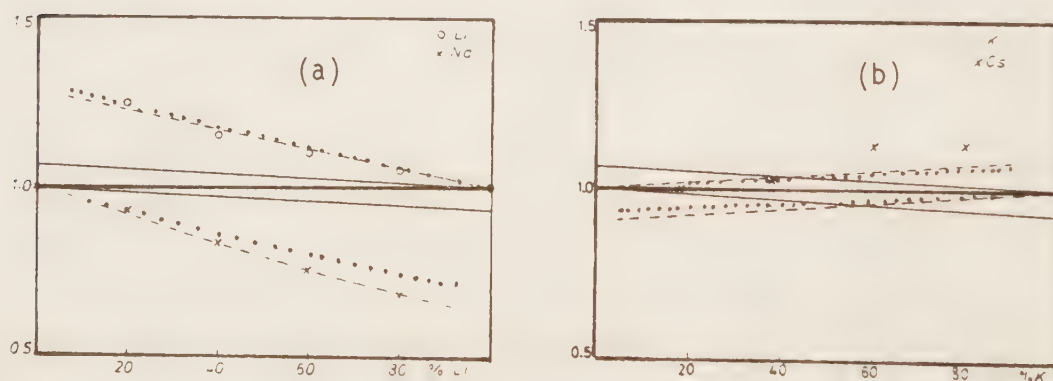


Figure 4. Diagrams showing competitive behaviour between a) (Li^+, Na^+) and b) (K^+, Cs^+) (from Figure V:2). — = ionic radius, ---- = U and = K.

reproduce the specificity, but it is possible to fit the experimental data with the other models. A similar diagram for (Na^+, Cs^+) showed no tendency for specificity, which is reflected in the equal values of the

potentials and binding constants for these ions.

In summary, the effects involved in the competitive binding of alkali counterions in this system appear to be small and of a local nature, which limits the use of the present models to explain the experimentally found affinity sequence.

6.5 Future Projects

The MC simulation performed to test the validity of the PB equation, mentioned previously in this section, can be considered to be the first step towards a molecular description of the lamellar system. At this moment several projects are in progress in our laboratory, involving both MC and MD simulations, in which the restrictions of the above model (6.2) are relaxed in one way or another.

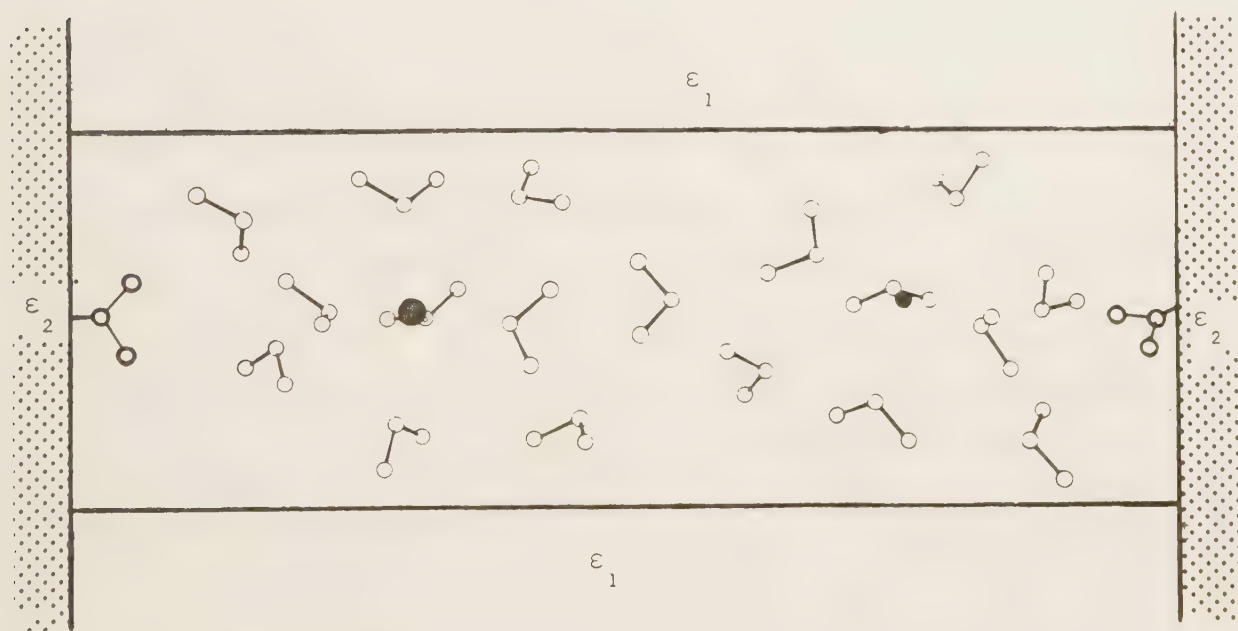


Figure 5. "A conceivable model of the lamellar solution region".

In order to obtain further insight into the local interactions determining the quadrupole splittings and the affinity sequence discussed above, the molecular nature of both the lamellar surface and the intervening solution must be taken into account. In Figure 5

a conceivable model of the lamellar solution region is illustrated.

In this model, the lamellar surface is represented by a carboxylate group, attached to the otherwise hard surface. The solution region is composed of the counterions and the water molecules. The interaction potentials between the carboxylate group on the one hand, and the ions and the water molecules on the other, must be determined. This is not a straightforward task, since it is difficult to describe the dissociation of a salt (e.g. $\text{-COO}^-\text{Na}^+$) quantum mechanically. Another problem is the increased number of variables in the pair potential surfaces, due to the complexity of the molecules. This means that a large number of quantum chemical calculations must be performed to give an accurate description of the interaction.

In the simulation of a model of this kind, one is probably (at present) limited to a rather small part of the solution region. Perhaps the "unit cylinder", sketched in Figure 5, is what one can afford. In practice this means: 2 carboxylate groups, 2 counterions (perhaps different) and 50-100 water molecules. The surroundings may be treated as a dielectric continuum, using the PB solutions previously described.

In this model MC and MD simulations can give information about:

- i) quadrupole coupling constants of the counterions
- ii) order parameters
- iii) hydration of counterions
- iv) ion specificity
- v) ordering of water molecules
- vi) diffusion coefficients
- vii) correlation times
- viii)

The idea of performing these kinds of simulations is indeed an exciting prospect for future work!

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Sternheimer shielding in molecules

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The effect of perturbing electric fields and electric-field gradients on the nuclear quadrupole coupling in molecules is investigated. The theory for the first-order effects is developed and it is shown that not only a perturbing field gradient but also a perturbing field, and higher terms, induce a finite field gradient at a nucleus in a molecule. The so-called Sternheimer (anti)shielding is thus considerably more complex in molecular than in atomic systems. The different shielding components have been calculated for HCl, HCN and NH_4^+ using a finite perturbation *ab initio* molecular orbital method. The calculated values are then used to rationalize experimentally determined ^{14}N quadrupole coupling constants in condensed media for HCN and NH_4^+ .

1. INTRODUCTION

In addition to the strong interaction between the nuclear charge and surrounding charges, nuclei with spin quantum number $I \geq 1$ also interact with the field gradient at the nucleus through their quadrupole moment. This interaction is the quadrupole coupling and is due to the second non-zero term in the multipole expansion of the nuclear charge distribution. Although this term gives rise to interactions more than six orders of magnitude smaller than the first, it plays an important role in several spectroscopic techniques, e.g. nuclear quadrupole resonance (N.Q.R.), nuclear magnetic resonance (N.M.R.), Mössbauer and microwave spectroscopy. The magnitude of the quadrupole coupling is determined by the nuclear quadrupole moment, eQ , and the electric field gradient tensor at the nucleus. This tensor is usually characterized by its largest principal component, $eq = \partial^2 V / \partial z^2$, and the asymmetry parameter

$$\eta = \left(\frac{\partial^2 V}{\partial x^2} - \frac{\partial^2 V}{\partial y^2} \right) / \frac{\partial^2 V}{\partial z^2}, \quad (1)$$

where V is the electrostatic potential and a principal coordinate system has been used. For molecular spectroscopists it is the field-gradient tensor that is the quantity of interest, since it gives valuable information about charge distributions and internal fields.

In the gas phase the field gradients have an intramolecular origin and reflect the electron distribution for a free molecule. In condensed phases, however, electric field gradients are also created by the surrounding molecules. This effect is particularly dramatic for systems where the free species have high enough symmetry around the nuclear centre to make the field gradient vanish.

For atoms and atomic ions Sternheimer realized at an early stage [1] that the field gradients created in condensed phases were due not only to external field gradients but also to a polarization of the electrons at the nucleus studied. Usually this induced field gradient gives the dominant contribution to the quadrupole coupling and the effect is called Sternheimer (anti)shielding. In a long series of papers [2] Sternheimer has developed the original ideas for spherically symmetrical systems. For a summary of the results one can consult the book by Lucken [3].

In molecular systems the effect of the Sternheimer shielding is often not so dramatic, since for free molecules the quadrupole coupling is usually non-zero. Exceptions to this rule are found for the central atom in molecular ions of cubic symmetry such as NH_4^+ , ClO_4^- or AsF_6^- . For the cases where the quadrupole coupling has been measured both in the gas and a condensed phase, they differ by approximately 10–20 per cent. By a correct understanding of the Sternheimer shielding effects, one could extract valuable information about the internal fields in the condensed phases from these differences.

In spherically symmetric systems the magnitude of the induced-field gradients can be determined by a single parameter, usually called γ_∞ , if only first-order effects are included. For molecules which have a lower symmetry, more parameters are needed in the description of the polarization effects. Furthermore, not only external electric field gradients but also electric fields and higher terms can induce finite gradients at the nucleus.

In the present paper we introduce the basic theory of Sternheimer shielding in molecules. The theory is then used to calculate, in an MO-SCF scheme, the different independent shielding components for ^{35}Cl in HCl and for ^{14}N in HCN and NH_4^+ . It is then shown how these components are able to account for the difference in the quadrupole coupling in gaseous and solid HCN. As a final example ^{14}N N.M.R. parameters of NH_4^+ are discussed.

2. THEORY

The interaction between the electrons in a molecule and an external change q_e is formally represented by the perturbation hamiltonian

$$\hat{H}' = \sum_i q_i V(\mathbf{r}_i), \quad (2)$$

where the sum is over all electrons in the molecule. When treating Sternheimer shielding it is convenient to obtain a series expansion of the potential around the nucleus of interest, which defines the origin of the coordinate system shown in figure 1. A spherical tensor expansion gives [4]

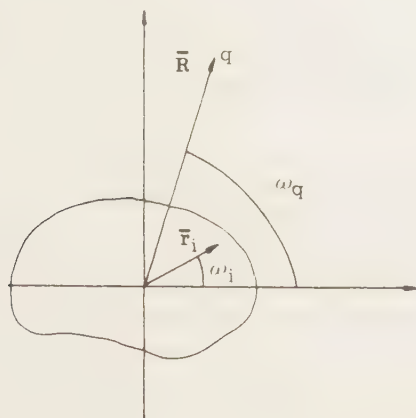
$$V(\mathbf{r}_i) = \frac{q_e}{|\mathbf{R} - \mathbf{r}_i|} = q_e \sum_L \frac{r_i^L}{R^{L+1}} \left(\frac{4\pi}{2L+1} \right) \sum_{M=-L}^L (-1)^M Y_{-M}^L(\omega_i) Y_M^L(\omega_q), \quad (3)$$

where $Y_M^L(\omega)$ are the normalized spherical harmonics. If one introduces

$$V_M^L(\text{ext}) = \frac{q_e}{R^{L+1}} \left(\frac{4\pi}{2L+1} \right)^{1/2} Y_M^L(\omega_q) \quad (4)$$

and

$$Q_M^L(\omega_i) = \sum_i q_i r_i^L \left(\frac{4\pi}{2L+1} \right)^{1/2} Y_M^L(\omega_i), \quad (5)$$



Definition of the coordinates used for the expansion in equation (3).

the perturbing hamiltonian can be written as a sum of contractions

$$\hat{H}' = \sum_L \sum_{M=-L}^L (-1)^M Q_{-M}^L(\omega_i) V_M^L(\text{ext}), \quad (6)$$

V_M^L are the derivatives of the potential defined as

$$\left. \begin{aligned} V_0^0 &= V; \quad V_0^1 = V_z; \quad V_{\pm 1}^1 = \mp \frac{1}{\sqrt{2}} (V_x \pm iV_y); \\ V_0^2 &= \frac{1}{2} V_{zz}; \quad V_{\pm 1}^2 = \mp \frac{1}{\sqrt{6}} (V_{xz} \pm iV_{yz}), \\ V_{\pm 2}^2 &= \frac{1}{2\sqrt{6}} (V_{xx} - V_{yy} \pm i2V_{xy}), \end{aligned} \right\} \quad (7)$$

so that V_M^0 , V_M^1 and V_M^2 are the potential, electric field and field gradient at the origin respectively. Q_M^L are the multipole moment operators. In the presence of this perturbation the molecular wave function is in first order changed to

$$|0\rangle' = |0\rangle + \sum_n |n\rangle \frac{\langle n|\hat{H}'|0\rangle}{E_0 - E_n}, \quad (8)$$

where $|0\rangle$ and $|n\rangle$ are unperturbed eigenvectors of H . In the perturbed state the expectation value of the nuclear field gradient is

$$\begin{aligned} \langle 0|V_M^2(\text{nuc})|0\rangle' &= \langle 0|V_M^2(\text{nuc})|0\rangle \\ &+ \sum_L \sum_{M'=-L}^L (-1)^{M'} \sum_n \{ \langle 0|V_M^2(\text{nuc})|n\rangle \langle n|Q_{-M'}^L|0\rangle \\ &+ \langle n|V_M^2(\text{nuc})|0\rangle \langle 0|Q_{-M'}^L|n\rangle \} V_{M'}^L(\text{ext}) / (E_0 - E_n), \end{aligned} \quad (9)$$

where the field-gradient operators are

$$V_M^2(\text{nuc}) = \left(\frac{4\pi}{5} \right)^{1/2} \sum_i q_i Y_M^2(\bar{r}_i) / r_i^3. \quad (10)$$

Formally one can write equation (9) in a spherical tensor notation including terms with $L \leq 2$

$$\langle V_M^2(\text{nuc}) \rangle' = \langle V_M^2(\text{nuc}) \rangle^0 + \sum_{M'} F_{MM'} V_{M'}^1(\text{ext}) + \sum_{M'} G_{MM'} V_{M'}^2(\text{ext}), \quad (11)$$

where

$$F_{MM'} = (-1)^{M'} \sum_n \{ \langle 0 | V_M^2(\text{nuc}) | n \rangle \langle n | Q_{-M'}^{-1} | 0 \rangle + \langle n | V_M^2(\text{nuc}) | 0 \rangle \langle 0 | Q_{-M'}^1 | n \rangle \} / (E_0 - E_n) \quad (12)$$

and

$$G_{MM'} = (-1)^{M'} \sum_n \{ \langle 0 | V_M^2(\text{nuc}) | n \rangle \langle n | Q_{-M'}^2 | 0 \rangle + \langle n | V_M^2(\text{nuc}) | 0 \rangle \langle 0 | Q_{-M'}^2 | n \rangle \} / (E_0 - E_n). \quad (13)$$

$F_{MM'}$ and $G_{MM'}$ are the molecular shielding factors describing the contributions to the nuclear field gradient due to the external field and field gradient respectively. For $F_{MM'}$ there are 15 independent components in the absence of any symmetry restrictions in the molecule, and for $G_{MM'}$ the corresponding number is 25. If molecular symmetry is taken into account the number of independent constants can be reduced. For example, if the molecule possesses an inversion centre at the nucleus, all $F_{MM'}$ are zero. The non-vanishing shielding factors for some important symmetries are summarized below:

spherical symmetry :

$$G_{00} = G_{\pm 1 \pm 1} = G_{\pm 2 \pm 2};$$

$$C_{\infty v}: F_{00}, F_{11} = -F_{-1-1} \text{ and } G_{00}, G_{11} = G_{-1-1}, G_{22} = G_{-2-2};$$

$$T_d: F_{1-1} = F_{-11} = \sqrt{2}F_{20} = -\sqrt{2}F_{-20} \text{ and } \\ G_{00}, G_{11} = G_{-1-1}, G_{\pm 2 \pm 2} = G_{00} - \frac{1}{2}G_{11}, G_{\pm 2 \mp 2} = G_{00} + \frac{1}{2}G_{11};$$

$$O_h: G_{00}, G_{11} = G_{-1-1}, G_{\pm 2 \pm 2} = G_{00} - \frac{1}{2}G_{11}, G_{\pm 2 \mp 2} = G_{00} + \frac{1}{2}G_{11}.$$

It is thus clear that it is more complicated to describe the influence of external perturbations on the field gradients for molecules, where it is necessary to include not only the external field gradient but also the external field, and at shorter distances higher derivatives of the potential. Except for molecules of high symmetry it does not seem feasible to determine the different components of the tensors $F_{MM'}$ and $G_{MM'}$. Equation (11) accounts for the electronic contribution to the induced field gradient. In addition to this the nuclear positions are also polarized by electrostatic effects. This mechanism is neglected below, but it will be discussed elsewhere.

3. CALCULATIONS

The components of the tensors F and G have been calculated for the chlorine nucleus in HCl and for the nitrogen nucleus in HCN and NH_4^+ . Using the *ab initio* MO-LCAO-SCF programme MOLECULE [5] the field gradient at the nuclear centre was calculated in the presence of an external unit charge. For a linear molecule, the change in field gradient relative to the free molecule, $\Delta V(\text{nuc})$,

is

$$\begin{aligned}\Delta V_0^2(\text{nuc}) &= F_{00}V_0^1(\text{ext}) + G_{00}V_0^2(\text{ext}), \\ \Delta V_{\pm 1}^2(\text{nuc}) &= F_{\pm 1\pm 1}V_{\pm 1}^2(\text{ext}) + G_{\pm 1\pm 1}V_{\pm 1}^2(\text{ext}), \\ \Delta V_{\pm 2}^2(\text{nuc}) &= G_{\pm 2\pm 2}V_{\pm 2}^2(\text{ext}),\end{aligned}\quad (14)$$

where the positive (or negative) signs are taken together.

By varying the distance between the centre and the external charge the contributions from the F and G terms were separated. Such a procedure was repeated for different orientations of the charge relative to the molecule, making it possible to determine the independent components of the tensors. An advantage with this finite perturbation approach is that it reveals the limit where higher order terms become important, either in the perturbation or the multipole expansion. Usually such higher order terms were found to be of importance at distances shorter than 5 Å (1 Å = 10^{-10} m). An exception was HCN with the charge perpendicular to the molecular axis, where a R^{-4} dependent term gave noticeable contributions up to $R = 20$ Å.

The basis sets used for the involved atoms consisted of contracted gaussian functions, and were of double zeta plus polarization type. They are listed in table 1. The use of basis sets of different sizes for HCl indicates that the hydrogen polarization function plays a more important role than the d-function on chlorine, as measured by the resulting accuracy of the quadrupole coupling

Table 1. Basis sets for H, C, N and Cl.

Atom	Basis sets		Exponent of polarization function
	Uncontracted	Contracted	
H (a)	(5, 1), (4, 1)†	<2, 1>	0.75
C (a)	(9, 5, 1)	<4, 2, 1>	0.80
N (a)	(9, 5, 1)	<4, 2, 1>	0.80
Cl (b)	(12, 9, 1)	<6, 4, 1>	0.60

† 5s, only HCl, s-exponents multiplied by 1.34.

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Table 2. Bond distances, energies and field gradients for HCl, HCN and NH_4^+ .

Molecule	Bond distances (Å)		Energy (a.u.)	Field gradients (a.u.)	
	R_1	R_2		Calculated	Experimental
HCl	1.275	—	−460.07913	3.48	3.66 (a)
HCN	1.066	1.153	−92.86700	−0.97	−1.25 (b)
NH_4^+	1.020	—	−56.54170	0	0

(a) From JONES, G., and GORDY, W., *Phys. Rev. A*, **136**, 1129 (1964). $Q(^{35}\text{Cl}) = -0.079 \times 10^{-28} \text{ m}^2$.

(b) From reference [8]. $Q(^{14}\text{N}) = 0.016 \times 10^{-28} \text{ m}^2$.

constant. In table 2 the intramolecular distances, calculated energies and unperturbed field gradients for HCl, HCN and NH_4^+ are given, together with experimentally determined field gradients. Table 3 shows the evaluated molecular shielding factors F and G for the chlorine and nitrogen nuclei in the three molecules. The calculated constant for the chloride ion is also included for comparison. The value 38 for the chloride ion is considerably smaller than previously obtained values [6]. This discrepancy is due to the fact that the basis set used in the present calculation is not flexible enough to account for all the polarization. One can thus expect a sizeable error in the absolute values of the coefficients in table 3, while the relative errors are considerably smaller.

Table 3. Calculated independent shielding components $F_{MM'}$ ($\text{\AA}^{-1}$) and $G_{MM'}$ for HCl, HCN, NH_4^+ and Cl^- .

	HCl	HCN	NH_4^+	Cl^-
F_{00}	-19	6.2		
F_{11}	-0.09	-2.5		
F_{1-1}			-i4.3	
G_{00}	39	-2	4.0	38
G_{11}	20	2.8	-10	
G_{22}	31	8		

A comparison between Cl^- and HCl reveals that no dramatic effects occur in the G tensor when the system is made neutral and the spherical symmetry is broken. In fact the field gradient along the molecular axis is not changed, while it is more difficult to polarize the electron cloud perpendicular to the molecular axis, probably a result of the H-Cl bond. A similar comparison between HCN and NH_4^+ reveals that chemical environment does not influence the order of magnitude of the shielding properties at the nitrogen nucleus.

A general conclusion for all three systems studied are that the effects of the electric field are the dominating ones at distances where the first-order treatment is valid. It is also clear that the orientation dependence is sizeable and has to be taken into account in a consistent treatment of Sternheimer shielding in molecular systems.

3.1. Field gradient at nitrogen in solid and gaseous HCN

For hydrogen cyanide the ^{14}N quadrupole coupling constant has been measured both in the gas phase by microwave spectroscopy [7, 8] and in the solid state by N.Q.R. [9]. Since the crystal structure of HCN is known [10] the calculated Sternheimer shielding factors can be tested against these experiments. In going from gas to solid the quadrupole coupling constant changes by 15–20 per cent and an interesting question is if these changes can be accounted for by the effect of the electric fields and field gradients created by surrounding molecules or if they are caused by specific interactions. According to the X-ray investigation [10] solid hydrogen cyanide occurs in two different crystallographic forms, one orthorhombic below and one tetragonal above the transition temperature

170.37 K. In both cases the HCN molecules are oriented along one of the crystallographic axis. In the tetragonal form the molecular axis is a fourfold symmetry axis making the asymmetry parameter η zero, while the asymmetry parameter in the orthorhombic form is non-zero.

Before equation (11) can be applied to calculate the medium effect on the quadrupole coupling constant, one has to calculate the electric field and field gradient caused by neighbouring molecules. We have chosen to approximate the charge distribution in HCN by point charges at the nuclear centres obtained from a Mulliken population analysis of our *ab initio* MO calculation. This is a rather arbitrary procedure, but it should be sufficiently accurate for the present purposes. A second difficulty is that the hydrogen cyanide crystal acts as a dielectric medium. Following Cohen and Reif [11] the dielectric effects are included by multiplying the final correction term with a polarization factor $(L\epsilon + L + 1)/(2L + 1)\epsilon$ where L is the rank of the tensor. The dielectric constant has been chosen as the square of the refractive index, $\epsilon = n^2 = 1.25^2$. The medium contribution to $e^2 qQ$ calculated from equation (11) and the coefficients F and G in table 3 is presented in table 4.

Table 4. Experimental and calculated coupling constants (MHz) for HCN in the gaseous state and in the two solid structures below (α) and above (β) the transition temperature. Asymmetry parameters in parenthesis.

	Gas	α	β	α/gas (per cent)	β/gas (per cent)
Experiment	-4.714 (0.0)	-4.018 (0.0085)	-3.890 (0.0)	85.2	82.5
Theory	-3.80 (0.0)	-3.18 (0.0014)	-3.16 (0.0)	83.6	83.1

The external field and field gradient at the central nucleus were calculated by summing over all molecules within a certain distance R . It was found that convergence is rapidly reached when R is extended and the main contribution thus comes from the near-neighbour molecules. From table 4 one can see that the calculation correctly predicts that the quadrupole coupling is smaller in the solid state than for the free molecule. The qualitative difference between the two crystalline phases is also correctly reproduced. This is noteworthy since from the simple argument that the medium effect is largest in the more dense phase one would reach the opposite conclusion. Table 4 also reveals that there is a quantitative agreement between the experimental and calculated relative changes when going from the free molecule to the solid state. Even though this quantitative agreement is to a large extent fortuitous, it shows that the electrostatic effects are large enough to account for the difference in the quadrupole coupling constant for the free molecule in a condensed phase.

Table 5 shows the nuclear field gradient separated into contributions from induced gradients due to external field and field gradient and from the charges themselves. There is a certain cancellation effect but it is clear that the external electric field is the most important of the three.

Table 5. Field gradient contributions in atomic units from 346 surrounding molecules in the high temperature form of solid HCN (cf. equation (11)).

Total	Field	Field gradient	Charge
ΔV_0^2 (nuc)	$F_{00} V_0^1$ (ext)	$G_{00} V_0^2$ (ext)	V_0^2 (ext)
0.219	0.282	-0.126	0.063

3.2. ^{14}N quadrupole coupling in the ammonium ion

An unperturbed ammonium ion possesses tetrahedral symmetry which makes the field gradient at the nitrogen nucleus vanish. A non-zero field gradient is thus due entirely to intermolecular interactions and the quadrupole coupling constant can be used as a probe of intermolecular fields.

In isotropic liquids the ^{14}N quadrupole coupling in NH_4^+ is the cause of the magnetic relaxation of the ^{14}N magnetization. According to Hertz [12], in water solution the magnetic relaxation of quadrupolar nuclei in symmetrical ions is due to the field gradients created by water dipoles in the solvation sphere. Combining this theory with the experimentally determined longitudinal relaxation time T_1 [13] for aqueous NH_4^+ one obtains an effective Sternheimer shielding of ± 20 . With the same model for the interactions the coefficients of table 3 give an effective Sternheimer shielding of -13 .

In a solid-state N.M.R. experiment Baily and Story [14] estimated the Sternheimer shielding for ^{14}N in $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ to 5. This was accomplished by a comparison with experiments on $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, from which the field gradient could be determined. The estimated value of 5 is in excellent agreement with the calculated field gradient term, but the whole analysis of the experiment neglects the field dependent terms for NH_4^+ .

4. CONCLUSIONS

It has been demonstrated that Sternheimer shielding effects are of the same order of magnitude in molecular as in atomic systems. The orientation dependence is however rather complicated which does not make it feasible to calculate shielding components for all but molecules of high symmetry. An important result of this work is that the external electric field usually produces the largest contribution to the induced field gradient for molecules with no inversion symmetry.

In the application HCN and NH_4^+ it has been shown that the calculated shielding components could account for the experimental observations in a semi-quantitative way. However, it should be noted that there are a number of uncertainties introduced into the calculations leading to a comparison with the experiments. There are sizable errors in the calculated shielding components. The values of the external field and field gradient is also approximate. The treatment of the medium effects in a continuum model can be discussed as well as the relevant value for the dielectric constant. The most important contributions to the induced field gradients come from molecules close to the nucleus studied and at these short distances higher order effects start to be of importance. In spite of all these difficulties the determination of a quadrupole coupling is a valuable method for probing electric fields and field gradients in condensed media.

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Nuclear quadrupole coupling and molecular deformations

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The importance of molecular deformations for the nuclear quadrupole coupling is determined. By considering a perturbing electrical field as causing the molecular deformation the change in the nuclear quadrupole coupling is related to force constants and derivatives of the dipole moment and the electrical field gradient at the nucleus with respect to a change in an internal coordinate. The various derivatives are explicitly determined for the systems HCl, HCN and NH_4^+ via MO-SCF calculations. The results for the NH_4^+ ion are discussed in relation to experimental determinations of ^{14}N quadrupole splittings in lyotropic liquid crystals.

1. INTRODUCTION

The electron-nuclear quadrupole interaction plays an important role in several spectroscopic techniques, e.g. nuclear quadrupole resonance (N.Q.R.), nuclear magnetic resonance (N.M.R.), Mössbauer and microwave spectroscopy. The nuclear quadrupole coupling constant, denoted $e^2 qQ/h$, is determined by the nuclear quadrupole moment, eQ , and by the electric field gradient at the nuclear centre, eq . In molecular spectroscopy it is the electric field gradients that carry the interesting information about the system studied, since they reflect the charge distribution around the nucleus. In the gas phase the field gradients have an intramolecular origin, but in condensed phases intermolecular interactions can also be of importance in determining the field gradients. This effect is particularly dramatic for systems where the intramolecular contribution vanishes by symmetry. This is, for example, the case for atomic systems in S states. It was realized by Sternheimer at an early stage [1] that an external field gradient interacts not only directly with the nuclear quadrupole moment but also through polarization of the electrons surrounding the nucleus. The effects of this electronic polarization in atomic systems has been characterized by the Sternheimer shielding parameter, usually written γ_∞ . The value of this parameter has been calculated for a number of atoms and atomic ions [2].

In a recent paper [3] we showed that Sternheimer's concept of an electron polarization contribution to the field gradients is also valid for molecular systems. Using first-order perturbation theory it was shown that the non-spherical symmetry of the molecular systems causes the polarization to be orientation dependent, i.e. several shielding parameters are required to characterize molecular systems. It was also found that an external electrical field gives non-zero contributions to the induced field gradients for molecules lacking an inversion centre. The

induced field gradients were expressed as

$$V_M^2(\text{nuc}) = \sum_{M'} F_{MM'} V_{M'}^1(\text{ext}) + \sum_{M'} G_{MM'} V_{M'}^2(\text{ext}), \quad (1)$$

where $F_{MM'}$ and $G_{MM'}$ are the shielding components describing the polarization due to the external electric field $V_{M'}^1(\text{ext})$ and field gradient $V_{M'}^2(\text{ext})$, respectively†. The non-vanishing components of the F and G tensors were calculated for the quadrupolar nuclei in H^{35}Cl , HC^{14}N and $^{14}\text{NH}_4^+$. It was shown that the components were of the same order of magnitude as in the corresponding atomic systems.

In addition to the electrons, the nuclear positions in a molecule are polarized by external electrostatic effects, i.e. the molecular geometry is changed. This deformation will give an additional contribution to the field gradients, and it can be treated as a shielding effect similar to the electronic one. In the present article we present a basic theory for the effect of distortions on the nuclear quadrupole coupling. Using a MO-SCF scheme the different independent shielding components are then determined for the quadrupolar nuclei in HCl , HCN and NH_4^+ . Finally the results are used to discuss some recent N.M.R. results in liquid-crystalline phases.

2. THEORY

It was shown in reference [3] that the contributions to the field gradients from the electronic polarization can be expressed by the use of two (reducible) tensors F and G (cf. equation (1)). The effect of distortions can be handled formally in the same way and it is shown below that equation (1) can be extended to

$$V_M^2(\text{nuc}) = \sum_{M'} (F_{MM'} + D_{MM'}) V_{M'}^1(\text{ext}) + \sum_{M'} G_{MM'} V_{M'}^2(\text{ext}), \quad (2)$$

where $D_{MM'}$ describes the contribution to the field gradient at the nucleus from a deformation due to a perturbing external electric field. The relationship between $D_{MM'}$ and other molecular constants will now be derived.

The potential energy of an unperturbed molecule can, for small deviations from the equilibrium geometry, be written as

$$V = V_0 + \sum_{i,j} \frac{1}{2} k_{ij} S_i S_j, \quad (3)$$

where V_0 is the potential energy at equilibrium and the force constants k_{ij} are the second derivatives of the potential with respect to the internal coordinates S_i . When an external electric field is imposed on the system it will interact with the molecular dipole moment and give an additional contribution to the potential energy. The dipole moment depends on the molecular geometry and it can be expanded in a Taylor series around its value at the equilibrium geometry

$$\langle \mu \rangle = \langle \mu \rangle_0 + \sum_i \left(\frac{\partial \langle \mu \rangle}{\partial S_i} \right)_0 S_i. \quad (4)$$

† In reference [3] V^1 was defined as minus the electrical field but the values of F in table 3 refer to the electrical field. In the present paper we continue to define V^1 as the electrical field. Furthermore, the relative signs between the dependent F and G components in [3] should be $C_{\alpha\gamma}$: $F_{11} = F_{-1-1}$; T_d : $F_{1-1} = -F_{-11} = -\sqrt{2}F_{20} = \sqrt{2}F_{-20}$; T_d and O_h : $G_{\pm 2 \pm 2} = G_{00} + \frac{1}{2}G_{11}$ and $G_{\pm 2 \mp 2} = G_{00} - \frac{1}{2}G_{11}$. Finally, $F_{11} = 0.09$ for HCl and $F_{1-1} = i4.3$, $G_{11} = 10$ for NH_4^+ in table 3.

Using a spherical tensor notation for the electrostatic interactions, the potential energy for the perturbed system is

$$V = V_0 + \sum_{ij} \frac{1}{2} k_{ij} S_i S_j - \sum_M (-1)^M \langle \mu_{-M} \rangle V_M^1(\text{ext}). \quad (5)$$

In a given field $V_M^1(\text{ext})$ † the molecule will find a new potential energy minimum. The geometrical parameters for this new minimum, i.e. the S_i 's, are obtained by minimizing the total energy in equation (5). The solution can be expressed formally as

$$\mathbf{S} = \mathbf{K}^{-1} \sum_M (-1)^M \boldsymbol{\mu}'_{-M} V_M^1(\text{ext}), \quad (6)$$

where $\mathbf{S}$ and $\boldsymbol{\mu}'_{-M}$ are column vectors with elements S_i and $(\partial \langle \mu_{-M} \rangle / \partial S_i)_0$, respectively, and $\mathbf{K}$ is the quadratic force constant matrix. One can note that by having an external electric field as the only perturbation, deformations will only occur for the infra-red-active internal modes. A Taylor expansion, similar to the one in equation (4), of the field gradients at the nucleus results in

$$\begin{aligned} \langle V_M^2(\text{nuc}) \rangle &= \langle V_M^2(\text{nuc}) \rangle_0 + \sum_i \left(\frac{\partial}{\partial S_i} \langle V_M^2(\text{nuc}) \rangle \right)_0 S_i \\ &= \langle V_M^2(\text{nuc}) \rangle_0 + \mathbf{V}'_M \mathbf{S}, \end{aligned} \quad (7)$$

where $\mathbf{V}'_M$ is the row vector formed by the field gradient derivatives. Substituting equation (6) in equation (7) one obtains

$$\langle V_M^2(\text{nuc}) \rangle = \langle V_M^2(\text{nuc}) \rangle_0 + \sum_{M'} D_{MM'} V_{M'}^1(\text{ext}), \quad (8)$$

where

$$D_{MM'} = (-1)^{M'} \mathbf{V}'_M \mathbf{K}^{-1} \boldsymbol{\mu}'_{-M'}. \quad (9)$$

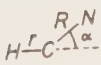
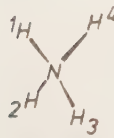
Equation (9) shows that the D components of equation (2) are determined by field gradient derivatives, force constants and dipole moment derivatives. There are a maximum of 15 independent D components, but this number is often substantially reduced by the molecular symmetry and by the fact that for small molecules one has only a limited number of internal infra-red-active modes.

3. CALCULATIONS AND RESULTS

To obtain a quantitative measure of the importance of molecular deformations for the nuclear quadrupole coupling we have determined the components of the D tensor for the three systems H^{35}Cl , HC^{14}N and $^{14}\text{NH}_4^+$. The three quantities that, according to equation (9), determine $D_{MM'}$ can be obtained either from a

† In reference [3] V^1 was defined as minus the electrical field but the values of F in table 3 refer to the electrical field. In the present paper we continue to define V^1 as the electrical field. Furthermore, the relative signs between the dependent F and G components in [3] should be $C_{\infty v}$: $F_{11} = F_{-1-1}$; T_d : $F_{1-1} = -F_{-11} = -\sqrt{2}F_{20} = \sqrt{2}F_{-20}$; T_d and O_h : $G_{\pm 2 \pm 2} = G_{00} + \frac{1}{2}G_{11}$ and $G_{\pm 2 \mp 2} = G_{00} - \frac{1}{2}G_{11}$. Finally, $F_{11} = 0.09$ for HCl and $F_{1-1} = i4.3$, $G_{11} = 10$ for NH_4^+ in table 3.

Table 1. Symmetry coordinates and quadratic force constants for HCl, HCN and NH_4^+ .

Molecule	Symmetry coordinates	Force constants/a.u. †
$\text{H}-\overset{\text{R}}{\text{Cl}}$	$S_1 = \Delta R$	$k_1 = 0.331$ (a)
	$S_1 = \Delta r$ $S_2 = \Delta R$ $S_3 = \alpha$	$k_1 = 0.402$ (b) $k_{12} = -0.0128$ $k_2 = 1.201$ $k_3 = 0.0595$ ‡
	$S_1 = \frac{1}{2}(R_1 - R_2 - R_3 + R_4)$ $S_2 = \frac{R_{\text{NH}}^{\text{eq}}}{\sqrt{2}} (\alpha_{23} - \alpha_{14})$	$k_1 = 0.339$ (c) $k_{12} = 0.00493$ § $k_2 = 0.0336$ ‡

† 1 a.u. = 1556.84 Nm^{-1} . ‡ a.u./ (rad^2) . § a.u./ (rad) .

(a) HERZBERG, G., 1950, *Spectra of Diatomic Molecules* (D. van Nostrand Company, Inc.).

(b) STREY, G., and MILLS, I. M., 1973, *Molec. Phys.*, **26**, 129.

(c) HARVEY, K. B., and MCQUAKER, N. R., 1971, *J. chem. Phys.*, **55**, 4396.

quantum-mechanical calculation or experimentally. We have chosen to calculate the dipole moment and field-gradient derivatives using molecular orbital methods. For the force constants, on the other hand, accurate experimental values are readily available. When evaluating these quantities, it is convenient to express the molecular deformations in the so-called internal symmetry coordinates. The advantage of doing so is that every S_i can be related to one of the irreducible representations of the molecular point group. Using standard group theoretical arguments one finds that the number of infra-red-active vibrations is one for HCl, four for HCN and six for NH_4^+ . Table 1 shows the symmetry coordinates and the related force constants for the three molecules studied.

The quantum-chemical calculations were performed with the MO-LCAO-SCF programme MOLECULE [4], where contracted gaussian functions are used as basis functions. The basis sets were of the double-zeta plus polarization type and they are listed in table 1 of reference [3]. Table 2 shows the equilibrium

Table 2. Bond distances, energies and field gradients for HCl, HCN and NH_4^+ .

Molecule	Bond distances/Å		Energy/a.u.	Field gradients/a.u.	
	R_1	R_2		Calculated	Experimental
HCl	1.275	—	-460.07913	3.48	3.66 (a)
HCN	1.066	1.153	-92.86700	-0.97	-1.25 (b)
NH_4^+	1.020	—	-56.54170	0	0

(a) JONES, G., and GORDY, W., 1964, *Phys. Rev. A*, **136**, 1129. $Q(^{35}\text{Cl}) = -0.079 \times 10^{-28} \text{ m}^2$.

(b) BHATTACHARYA, B. N., and GORDY, W., 1960, *Phys. Rev.*, **119**, 144. $Q(^{14}\text{N}) = 0.016 \times 10^{-28} \text{ m}^2$.

Table 3. Calculated dipole moment derivatives (e or e/(rad)). Experimental values in parentheses.

	HCl (a)	HCN (b)	NH ₄ ⁺
$\frac{\partial}{\partial S_1} \langle \mu_0 \rangle$	0.209 (0.193)	0.296 (0.214)	1.699
$\frac{\partial}{\partial S_2} \langle \mu_0 \rangle$	—	0.162 (−0.117)	0.544
$\frac{\partial}{\partial S_3(x)} \langle \mu_1 \rangle$	—	−0.395 (−0.313)	—

Experimental values :

(a) KAISER, E. W., 1970, *J. chem. Phys.*, **53**, 1686.(b) HYDE, G. E., and HORNIG, D. F., 1952, *J. chem. Phys.*, **20**, 647.

geometries used, together with the calculated values of the energies and field gradients. For comparison the experimental field gradients are also listed. The dipole moment and field-gradient derivatives were calculated by varying bond lengths and bond angles in finite steps along the symmetry coordinates. Table 3 shows calculated and available experimental dipole moment derivatives. For HCl the agreement between calculated and experimental values is excellent. For HCN the calculated derivatives are up to 40 per cent too large. Moreover, the calculated relative signs are not consistent with the experimental data. This discrepancy between theory and experiment remains when the basis set is enlarged [5, 6] and it seems to be an open question whether the discrepancy is due

Table 4. Calculated field gradient derivatives (a.u. or a.u./(rad))†. Experimental values in parentheses.

	HCl (a)	HCN	NH ₄ ⁺
$\frac{\partial}{\partial S_1} \langle V_0^2 \rangle$	1.093 (1.104)	0.0586	—
$\frac{\partial}{\partial S_2} \langle V_0^2 \rangle$	—	0.404	—
$\frac{\partial}{\partial S_3(x)} \langle V_1^2 \rangle$	—	0.278	—
$\frac{\partial}{\partial S_1} \langle V_2^2 \rangle$	—	—	i0.580
$\frac{\partial}{\partial S_2} \langle V_2^2 \rangle$	—	—	−i0.119

† 1 a.u. = 9.7175×10^{21} Vm^{−2}.

Experimental values :

(a) KAISER, E. W., 1970, *J. chem. Phys.*, **53**, 1686.

Table 5. Calculated independent D -components $D_{MM'}$ ($\text{\AA}^{-1}$). The corresponding Sternheimer factors $F_{MM'}$ in parentheses.

	HCl	HCN	NH_4^+
D_{00}	1.3 (−19)	0.19 (6.2)	—
D_{11}	—	−7.0 (−2.5)	—
D_{1-1}	—	—	−i2.5 (i4.3)

$$1 \text{ \AA} = 10^{-10} \text{ m.}$$

to a misinterpretation of the experimental data or to inadequacies in the calculations and therefore probably in the Hartree–Fock approximation. In determining the D factors we have consistently used the calculated dipole moment derivatives in spite of this problem.

In table 4 the field gradient derivatives, with respect to changes in the symmetry coordinates, are given. It is again seen that the agreement between calculated and experimental values is very good for HCl. The calculated value also agrees with a previous calculation by Huo [7]. The independent components of the D tensor are listed in table 5, where the corresponding electronic shielding factors (Sternheimer factors) are given in parenthesis of comparison. It is seen that an electric field parallel to a bond affects the electron cloud much more than the nuclear positions. A field perpendicular to the HCN molecular axes has, on the other hand, the effect of creating an induced field gradient at the nitrogen nucleus by bending the molecule rather than by distorting the electron distribution. These results are physically quite reasonable, since a molecular geometry is most easily distorted by bending, and the electrons are usually more polarizable along, rather than perpendicular to, bonds. In HCl and NH_4^+ the contributions to the electric-field gradients from distortion and electronic polarization are seen to be counteractive while for HCN they enhance one other.

4. QUADRUPOLE SPLITTINGS IN LYOTROPIC LIQUID CRYSTALS

Although a distortion certainly affects the quadrupole coupling, relatively few experimental studies have been made which relate these two quantities. An exception is found in studies of symmetrical XY_4 ions in lyotropic liquid crystals. In such an anisotropic system one can observe a quadrupole splitting in the N.M.R. spectrum of ^{14}N for NH_4^+ [8–10] and for $\text{N}^+(\text{CH}_3)_4$ [8, 11], of ^{11}B for BF_4^- [12] and of ^{35}Cl for ClO_4^- [13]. The NH_4^+ ion has been particularly extensively studied. The theoretical analysis of these experiments have been based on the theory of Bailey *et al.* [12] which relates quadrupole splittings of symmetrical molecules and ions to molecular distortions. The present calculations have relevance to the theory of Bailey *et al.* in two respects.

Bailey *et al.* estimate, by comparison with the quadrupole coupling in ammonia, that for a deformation of the NH_4^+ ion of one degree along a bending coordinate of T_2 symmetry, the quadrupole coupling becomes 341 kHz. In our explicit SCF calculations on a deformed NH_4^+ ion the corresponding figure is 40 kHz. There is thus an order of magnitude difference between the two values and this is of considerable importance in a quantitative analysis.

The quadrupole splitting Δ observed in lyotropic liquid crystals represents an average over several molecular sites [14] so that

$$\Delta = \left| \sum_i p_i \Delta_i \right|, \quad (10)$$

where p_i is the fraction of the species studied in site i and Δ_i is the effective quadrupole splitting, positive or negative, for that site. For both lamellar and hexagonal liquid crystalline phases the symmetry is high enough to ensure that for each site with a certain electrical field E there is an equivalent site with electrical field $-E$. Distortions due to electrical fields thus do not contribute to the observed quadrupole splitting. These are caused by higher order effects and interactions of a non-electrostatic origin. One can thus expect that the distortion of the NH_4^+ ion in liquid crystals can be greater than the distortions revealed by the N.M.R. experiment.

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MONTE CARLO SIMULATIONS OF THE ELECTRIC FIELD GRADIENT
FLUCTUATION AT THE NUCLEUS OF A LITHIUM ION IN DILUTE AQUEOUS
SOLUTION.

by

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Abstract

The field gradient fluctuation at the Li^+ nucleus in dilute aqueous solution is calculated via Monte Carlo simulations of $\text{Li}^+ + n \text{H}_2\text{O}$ clusters ($n=6, 50$ and 150). The intermolecular potentials and the lithium field gradient function, necessary for the simulations, are based on ab initio quantum mechanical calculations. It is found that the dominating contribution to the field gradient fluctuation at the lithium nucleus, comes from the water molecules in the first shell. Furthermore, it is the lateral displacement of these molecules, that causes the largest fluctuation. The contribution from the rotation of a water molecule is of minor importance. The field gradient at a lithium nucleus, arising from a water molecule, is badly described in a simple electrostatic model.

1. INTRODUCTION

The Monte Carlo (MC) simulation technique has turned out to be a valuable tool in the study of equilibrium properties of liquids. The MC technique has been widely used as a test on different physical theories [1,2], and it has also been used with accurate intermolecular potentials to predict properties of real fluids [3,4]. This work, in which a quantity relevant to the nuclear magnetic resonance (NMR) relaxation of quadrupolar nuclei in aqueous solution is calculated, will give an example of the latter case.

The quadrupole relaxation technique has been extensively used in the study of counter- and co-ions in surfactant as well as in biological systems. The water structure in inhomogeneous systems, i.e. the water orientation close to a macromolecular surface, have also been investigated using quadrupole relaxation techniques [5-8].

For several atomic nuclei, with spin quantum number $I > 1/2$, the NMR relaxation is for the main part caused by the interaction between the nuclear electrical quadrupole moment and the fluctuating electric field gradient, arising from all charges surrounding the nucleus. Attempts to relate the experimentally determined relaxation rate to molecular properties gives a product of two unknown quantities. One is the field gradient fluctuation, and the other a correlation time, specifying the time-scale of the fluctuation. The former quantity is accessible from Monte Carlo simulations, while the latter demands a statistical method, where time is explicitly incorporated, i.e. a Molecular Dynamics simulation.

In this work the field gradient fluctuation at the nucleus of a Li^+ ion in a model, mimicking an infinitely diluted aqueous solution, is calculated. In order to investigate its sensitivity to different simulation conditions, the number of particles and the volume they occupy are varied. Another aspect which is thoroughly examined, is the origin of the fluctuation. Several models [9-13] have been proposed to explain the fluctuation, and some of them are scrutinized with

respect to the Monte Carlo results.

It seems appropriate to start with a brief review of the theory of quadrupolar relaxation of ions in aqueous solution, and also to give the basic ideas pertinent to the MC simulations. These two sections are followed by the computational details, such as the origins and forms of the intermolecular potentials and field gradient function, as well as the simulation conditions. The results are then summarized and discussed with respect to other models. A critical discussion of possible errors inherent in the present approach is also included.

2. QUADRUPOLEAR RELAXATION [14,15]

In a NMR experiment a collection of nuclear spins, e.g. the lithium nuclei in a dilute aqueous LiCl solution, is subjected to a strong static magnetic field, in which the sample acquires a net equilibrium magnetization. The equilibrium is then perturbed by applying a short intense radiofrequency pulse and the relaxation back to the equilibrium Boltzmann distribution of spins over nuclear Zeeman levels is observed. This relaxation process is induced by time dependent interactions between the nuclei and their environment, and can therefore yield information about molecular interactions and dynamics. For nuclei with spin $I > 1/2$, e.g. ${}^7\text{Li}$ with $I = 3/2$, the relaxation is due mainly to the interaction of the nuclear electric quadrupole moment with the fluctuating electric field gradient present at the position of the nucleus [16]. In the case of a Li^+ ion surrounded by water, the field gradient at the ionic nucleus is generated by the charges of the ionic electron cloud and of the water molecules. The field gradient is described by a symmetric, traceless, second-rank tensor $\mathbf{V}$, with components

$$V_{\alpha\beta} = \frac{\partial^2 V}{\partial \alpha \partial \beta} \quad (1)$$

where $\alpha, \beta = x, y, z$ and V is the electric potential. The field gradient at the nucleus reflects the symmetry of the environment. If, for example, the nucleus is situated at the intersection of two or more at least threefold rotation axes, as for octahedral or tetrahedral symmetry, then the field gradient vanishes.

The time dependent part of the semiclassical spin Hamiltonian, which is responsible for quadrupolar relaxation, may be written

$$\begin{aligned} \hat{H}_Q(t) &= \hat{\mathbf{Q}} : \mathbf{V}(t) = \sum_{k=-2}^2 (-1)^k \hat{Q}_{-k} V_k(t) = \\ &= \frac{eQ}{2I(2I-1)} \sum_{k=-2}^2 (-1)^k \hat{A}_{-k} V_k(t) \end{aligned} \quad (2)$$

where the scalar contraction has been written in terms of irreducible tensor components, and where the last equality follows from the Wigner-Eckart theorem [17]. $\hat{A}_k$ is a second-rank irreducible spin operator component, eQ denotes the nuclear electric quadrupole moment, and the irreducible field gradient components are

$$\begin{aligned} V_0 &= \frac{\sqrt{6}}{2} V_{zz} \\ V_{\pm 1} &= \mp (V_{xz} \pm iV_{yz}) \\ V_{\pm 2} &= \frac{1}{2} (V_{xx} - V_{yy} \pm 2iV_{xy}) \end{aligned} \quad (3)$$

In the expression for the relaxation rate,

$$R = \frac{2I+3}{I^2(2I-1)} \left(\frac{eQ}{\hbar}\right)^2 \frac{1}{40} \int_{-\infty}^{\infty} e^{-i\omega t} \langle \mathbf{V}(0) : \mathbf{V}^*(t) \rangle dt \quad (4a)$$

$$\langle \mathbf{V}(0) : \mathbf{V}^*(t) \rangle = \sum_{k=-2}^2 (-1)^k \langle V_k(0) V_{-k}^*(t) \rangle \quad (4b),$$

the effect of the surrounding charge distribution enters through so-called spectral densities, $J_{k1}(\omega)$, which are Fourier transforms of field gradient correlation functions

$$J_{k1}(\omega) \equiv \frac{1}{2} \int_{-\infty}^{+\infty} dt e^{-i\omega t} \langle V_k(0) V_1^*(t) \rangle \quad (5a)$$

where the angular brackets denote an equilibrium ensemble average. If the Hamiltonian describing the molecular motion is rotationally invariant, which is the case in an isotropic system, then Hubbard's theorem [18] states that

$$J_{k1}(\omega) = \delta_{k,-1} (-1)^k J_{00}(\omega) \quad (5b)$$

so that only the V_{zz} component enters the relaxation equations. If furthermore the molecular motions responsible for the time dependence in $V_{zz}(t)$ are fast relative to the inverse resonance frequency $1/\omega_0$ (as ω_0 is of the order 10^8 rad/s, this condition is certainly satisfied in an aqueous electrolyte solution at room temperature), then the exponential in Eq. (4a) can be set equal to unity, and the following expression for the relaxation rate R may be derived

$$R = \frac{1}{4} \frac{(2I+3)}{I^2(2I-1)} \left(\frac{eQ}{\hbar}\right)^2 J_{00}(0) \quad (6)$$

In the absence of detailed knowledge about the water motion, it is convenient to define an effective correlation time through

$$\tau_{\text{eff}} \equiv J_{00}(0) / \langle V_0^2(0) \rangle \quad (7)$$

It should be noted however, that only for an exponentially decaying correlation function, which is appropriate for e.g. isotropic rotational diffusion, is τ_{eff} a purely dynamical quantity. For more complex motions τ_{eff} will also depend on geometrical factors.

Equations (2-7) can now be combined and we obtain

$$R = \frac{3}{8} \frac{(2I+3)}{I^2(2I-1)} \left(\frac{eQ}{\hbar}\right)^2 \langle V_{zz}^2 \rangle \tau_{\text{eff}} \quad (8)$$

where the argument of V_{zz} has been dropped for simplicity. In the following we calculate the experimentally inaccessible field gradient fluctuation, $\langle V_{zz}^2 \rangle$, via a Monte Carlo simulation, thereby making it possible to deduce the correlation time from the measured relaxation rate.

Finally, a remark about the choice of coordinate axes is in order. Considering the interaction of a nucleus characterized by spin and

electric quadrupole moment, with its surrounding charge distribution, the z-direction is defined by the external static magnetic field. But the nuclear environment is isotropic, so that the choice of z-axis is arbitrary for purposes of calculating $\langle V_{zz}^2 \rangle$. In the MC simulation we evaluate $\langle V_{zz}^2 \rangle$ with respect to a fixed axis by generating configurations corresponding to the members of an equilibrium ensemble. However, one could equally well transform to the particular field gradient principal axes system for each member of the ensemble and then perform an isotropic orientational average to obtain

$$\langle V_{zz}^2 \rangle = \frac{2}{15} \langle \mathbf{V} : \mathbf{V} \rangle \quad (9)$$

where, on the right-hand side, a scalar quantity is averaged.

3. THE MONTE CARLO SIMULATION TECHNIQUE

The MC procedure is a general method to solve integrals of high dimensionality, such as the statistical mechanical average of a physical quantity, say the field gradient fluctuation, that reads

$$\langle V_{zz}^2 \rangle = \int_{\{X\}} V_{zz}^2(X) e^{-U(X)/kT} dX / Z \quad (10)$$

where Z is the configurational integral,

$$Z = \int_{\{X\}} e^{-U(X)/kT} dX \quad (11)$$

In Eqs. (10) and (11) X is a short-hand notation for the coordinates of all molecules in the system, and $U(X)$ is their total potential energy.

The standard Monte Carlo method would be to pick out one configuration of the water molecules at random, calculate the properties of interest for that configuration, and multiply by the appropriate Boltzmann factor. Repeating this procedure many times, adding the terms and normalizing, one will hopefully reach convergence. However, since the integrands in Eqs. (10) and (11) are rapidly varying functions, very few of the randomly chosen configurations will have any appreciable weight, resulting in a very poor convergence in such a procedure. To circumvent this problem one is forced to use an "importance sampling" of configurations. This method was introduced in the early 50's by Metropolis et al. [19], and is based on the generation of a so-called Markov chain. The advantage with the importance sampling is that a configuration X_i is chosen according to its statistical weight. This enables Eq. (10) to be written as

$$\langle V_{zz}^2 \rangle = \frac{1}{M} \sum_{i=1}^M V_{zz}^2(X_i) \quad (12)$$

where M is the total number of configurations. In practice the system is first "equilibrated" by generating a large number of configurations,

so that the total energy or some other relevant property is seen to fluctuate around some stable mean value. Then new configurations are generated and the properties of interest are calculated according to Eq. (12). Figure 1 shows a typical behaviour of the total energy for the system $\text{Li}^+ + 150 \text{H}_2\text{O}$ as a function of the number of generated configurations. The vertical bars in the figure indicate the configurations on which the calculation of the statistical averages are based (the analysis step).

4. COMPUTATIONAL DETAILS

In order to calculate the field gradient fluctuation via a Monte Carlo simulation, one needs explicit expressions for the potential energy of the system, and for the field gradient at the lithium nucleus. For simplicity, these quantities are approximated as sums of pair-wise additive interactions. The effects of ignoring higher-order terms have been shown to introduce a 10% error in the solvation energy of Li^+ [20]. The effects on the distribution of water molecules around the ion and on the field gradient are discussed at some length below.

4.1 The Energy Surface

Using the assumption of pair-wise additivity the interaction energy of a system of one lithium ion and N water molecules in a configuration X_i , can be written as

$$\Delta E(X_i) = \sum_{k=1}^N \Delta E^{WW}(x_k, x_1) + \sum_{k=1}^N \Delta E^{IW}(x_k) \quad (13)$$

Here $\Delta E^{WW}(x_k, x_1)$ is the interaction energy between two water molecules at positions x_k and x_1 respectively. $\Delta E^{IW}(x_k)$ is the corresponding ion-water interaction energy. The pair-potentials used in this work, have both been obtained from accurate quantum chemical calculations fitted to analytical expressions. The water dimer potential has been determined by Matsouka et al. [21], while the ion-water potential was obtained in this work. The latter is based on ab initio MO-LCAO-SCF calculations of 77 relative orientations of the ion and a water molecule, using an extended basis set. The basis set and the orientations chosen closely follow the work by Clementi and Popkie [22]. The main difference between the present basis set and that used by Clementi and Popkie, is that we have included a d-function on Li^+ with an exponent of 3.0, in order to account for polarization effects. The energies of the isolated species are -7.23605 a.u. and -76.05511 a.u. for the lithium ion and water respectively. The most stable conformation,

which is a planar complex with C_{2v} -symmetry and the oxygen atom pointing towards the ion, has an energy of -83.34606 a.u., i.e. the interaction energy is -144.1 kJ/mol. The Li-O distance for that complex is 1.88 Å. In the calculations the water molecule geometry was held fixed at its experimental values, the O-H distance was 0.957 Å and the H-O-H angle was 104.5° .

The calculated energies between H_2O and Li^+ were fitted to a function of the form

$$\Delta E^{IW} = \frac{Q_O}{R_O} + Q_H \left(\frac{1}{R_{H1}} + \frac{1}{R_{H2}} \right) + \frac{A_O}{R_O^2} + A_H \left(\frac{1}{R_{H1}^2} + \frac{1}{R_{H2}^2} \right) + \frac{B_O}{R_O^6} + B_H \left(\frac{1}{R_{H1}^6} + \frac{1}{R_{H2}^6} \right) + \frac{C_O}{R_O^{12}} + C_H \left(\frac{1}{R_{H1}^{12}} + \frac{1}{R_{H2}^{12}} \right) \quad (14)$$

The distances introduced in Eq. (14) are defined in Figure 2, and the parameter values obtained from the linear least-squares fit are listed in Table 1. Thus, ΔE^{IW} consists of a Coulomb interaction, an ion-dipole term and a Lennard-Jones term. The charges on the oxygen and hydrogens were taken from a Mulliken population analysis from a calculation on the isolated water molecule. A weight factor,

$$w_i = 1 + 20 \cdot e^{-(\Delta E_i^{IW} - \Delta E_{min}^{IW})/kT} \quad (15)$$

used by Jorgenson [23], has been used in order to improve the fit in the energy minimum. The error sum of the fit, σ , defined as

$$\sigma^2 = \frac{\sum_{i=1}^{77} w_i (\Delta E_{fit}^{IW} - \Delta E_{calc}^{IW})^2}{\sum_{i=1}^{77} w_i} \quad (16)$$

was ~ 5 kJ/mole. The corresponding value for the water-water potential obtained by Matsouka et al. [21] was ~ 1 kJ/mole.

4.2 The Field Gradient Function

Besides the energies, the field gradient tensor at the lithium nucleus was also determined in each of the ab initio calculations. Like the interaction energy, the total field gradient V_{zz} is approximated as a sum of contributions from single water molecules, i.e.

$$V_{zz} = \sum_{i=1}^N V_{zz}^{IW}(x_i) \quad (17)$$

where V_{zz}^{IW} is the field gradient caused by a water molecule at position x_i .

In order to estimate the error introduced by assuming a pair-wise additive field gradient, a few ab initio calculations were performed on the $\text{Li}^+ + 2\text{H}_2\text{O}$ system. The positions of the water molecules around the ion are shown in Figure 3, and the calculated field gradients are listed in Table 2, with the corresponding values obtained using the pair-approximation, Eq. (17), in parenthesis. In Table 2 the interaction energies, ΔE , are also given, where $\Delta E = E(\text{Li}^+, \text{W1}, \text{W2}) - E(\text{Li}^+) - 2E(\text{W})$. There is only one of the configurations, i.e. Figure 3c, which differs significantly from the pair-approximation value. It is not likely that this will cause any substantial error above a 5 - 10 % level in the field gradient, since the failing V_{zz} -component is small, and when the effects for several water molecules are added, the discrepancies may cancel. Furthermore, in an aqueous solution the average $\text{Li}^+ - \text{O}$ distance will be somewhat larger than the one used in the above test calculations. This will of course improve the pair-approximation, Eq. (17).

The 77 field gradients were fitted to an analytical expression of the following form:

$$\begin{aligned}
 V_{zz}^{IW} = & \left[\frac{D_0}{R_0^3} + \frac{E_0}{R_0^4} + \frac{F_0}{R_0^5} \right] S_0^2(\Theta_0) + \\
 & \left[\frac{D_H}{R_{H1}^3} + \frac{E_H}{R_{H1}^4} + \frac{F_H}{R_{H1}^5} \right] S_0^2(\Theta_{H1}) + \\
 & \left[\frac{D_H}{R_{H2}^3} + \frac{E_H}{R_{H2}^4} + \frac{F_H}{R_{H2}^5} \right] S_0^2(\Theta_{H2})
 \end{aligned} \tag{18}$$

where

$$S_0^2(\Theta_I) = \frac{1}{2} (3 \cos^2 \Theta_I - 1) \tag{19}$$

The angles in Eq. (18) are defined in Figure 2, and the fitted parameters are shown in Table 1. The error sum of the fit (see Eq. (16)) was 0.0019 a.u., which can be compared to the field gradient for the most stable complex, 0.0119 a.u.

4.3 The Monte Carlo Simulations

Since we have tried to mimic a lithium ion in water at infinite dilution, our Monte Carlo "box" consisted of a spherical cavity with a lithium ion fixed in the center, surrounded by 6, 50 and 150 water molecules respectively. The radius of the sphere was changed in order to investigate how the density and the boundary conditions affected the field gradient. All simulations were undertaken at a system temperature of 300 K, and the maximum translation and rotation of the water molecules were 0.3 Å and 10.3° respectively in all directions.

A typical Monte Carlo simulation started with an equilibration, where 300.000 - 1.500.000 configurations were generated, depending on the system size. After equilibration, new configurations were generated and the coordinates of the water molecules were stored for subsequent analysis consisting of: i) a calculation of the radial distribution of water molecules around the ion, ii) an analysis of the geometry of the first hydration shell, iii) a calculation of the field gradient and its fluctuation arising from all molecules and iv) a calculation of the field gradients from individual molecules and groups of them.

5. RESULTS AND DISCUSSION

This section is divided into five subsections starting with a discussion of the water-lithium radial distribution function. In the two following sections, quantum mechanical calculations of the nuclear field gradient and the Monte Carlo simulation of its fluctuation are presented. These parts are followed by a comparison between the present results for the field gradient fluctuation and the theories by Devereil [9], Hertz [11] and Friedman [13]. Finally we discuss approximations in the present treatment and possible refinements of the model.

5.1 The Water-Lithium Radial Distribution Function

A test of the accuracy of the Monte Carlo results, is to compare the obtained radial distribution of water molecules around the Li^+ ion with experimental data taken from X-ray and neutron diffraction experiments. Since the concentration of ions in this work resembles infinite dilution, it is not possible to make direct comparison with experiment. However, data from solutions with finite concentrations may anyway give a hint of the quality of our simulation results.

Enderby and Neilson have in a review article [25] collected X-ray data on a number of different cations and anions, together with their own results obtained from neutron diffraction measurements. Some of these data are listed in Table 3, together with the results from the present MC simulations. The agreement between experiment and our theoretical predictions is rather good. For example, the average hydration number found in the simulations is just above 5 compared to the experimental results ranging from 4 to 6. The maxima in the oxygen and hydrogen radial distribution functions are in agreement to within 0.1 Å, (see Table 3). Our results do also agree with the ones found by Clementi and Barsotti from simulations of $\text{Li}^+ + 200 \text{ H}_2\text{O}$ [26].

Since the mean hydration number is about five, the average arrangement of the water molecules in the first shell can not be of cubic symmetry. By "cubic" is here meant the symmetry of the arrangement of water oxygens. If these are situated tetrahedrally or octahedrally around the Li^+ ion, and since the major contribution to the field gradient comes from the oxygens (see below), the field gradient will be close to zero. This is not so for a trigonal bipyramidal arrangement of the oxygens, since they themselves give a non-zero contribution to the field gradient.

Thus, the MC results reveal that at least part of the contribution to the field gradient fluctuation, comes from a mean non-cubic arrangement of water oxygens. This result is interesting, since some models dealing with the origin of the fluctuation, consider the first shell as consisting of either four or six water molecules oriented in a mean cubic arrangement [10,11,13].

In order to analyze the geometry of the first shell in more detail, we have also calculated the mean O-Li-O angles (see Figure 2) for the molecules in the first shell. The probability for different angles have been plotted in Figure 4. Histogram (a) represents a total average calculated during the whole MC simulation of $\text{Li}^+ (\text{H}_2\text{O})_{150}$ with an average hydration number of 5.5. The second histogram (b) is a subaverage obtained during a smaller part of the simulation when the hydration number was close to six. The second histogram shows two maxima, at 180° and 90° , and their relative intensities, 1:4, are in agreement with an octahedral arrangement of the water oxygens. The total average (a) is clearly a mixture of different hydration numbers not corresponding to any definite water arrangement around the lithium ion.

To summarize, the mean hydration number is ranging between four and six, and the mean geometry of the first shell can then be seen as a mixture of tetrahedral, trigonal bipyramidal and

octahedral symmetry (i.e. for the water oxygens), rather than one particular of these.

5.2 Quantum Chemical Calculation of the Field Gradient

Before proceeding to simulate a large sample of water molecules and a Li^+ ion, it may be worthwhile to consider the field gradient obtained in the quantum mechanical calculations with fixed complex geometry. It is interesting to see whether the field gradient at the lithium nucleus is due to purely electrostatic effects or other mechanisms, such as higher order polarization or overlap effects. With overlap effects is meant the distortion of the Li^+ electron cloud, which occurs when a water molecule and an ion collide. The distortion is a consequence of the Pauli exclusion principle.

The electrostatic interactions are generally treated in a perturbational approach [27]. If we treat the water molecule, which is our perturbation, as a dipole, it will give rise to an electric field, field gradient ...and so on at the lithium nucleus. The perturbation treatment of the electrostatic interactions is usually carried only to first order, and due to the spherical symmetry of the ion the main term will be the field gradient perturbation. This means that the perturbed lithium field gradient may be written as

$$V_{zz}^{\text{Li}} = (1 + \gamma) V_{zz}^{\text{pert}} \quad (20)$$

where V_{zz}^{pert} is the field gradient at the nucleus due to the perturbation itself. The coefficient γ is the so-called Sternheimer (anti)shielding factor [28]. Eq. (20) is valid as long as higher order terms in the perturbation treatment can be neglected, and if not, one will find that γ is R-dependent (R being the distance between Li^+ and the perturbation). For Li^+ we have found, by performing SCF-calculations on a Li^+ ion and a dipole, that γ is independent of R for distances larger

than 3 a.u., with a value of -0.29, which agrees to within a few percent with earlier calculations [29]. Thus, we can see that the first order theory predicts the induced field gradient very well, so if we try to mimic a water molecule by a dipole or as three point charges at the positions of the atoms, we will find that first order theory gives the same result as a n :th order perturbation calculation.

However, if we compare the field gradient obtained with a non-polarizable dipole, as above, with that obtained in an ab initio SCF calculation with a "real" water molecule, the result will be very much different. Figure 5 shows the field gradient at the Li^+ nucleus arising from: (a) SCF calculations on a $\text{Li}^+ + \text{H}_2\text{O}$ complex and b) an ideal dipole multiplied with $(1 + \gamma_{\text{Li}})$, for various distances between the ionic nucleus and the dipole and water oxygen respectively. When replacing the water molecule with a point dipole the latter has been placed at the water oxygen coordinate. The two curves happen to cross very close to the average Li-O distance found in aqueous solution, but it should be noted that the curves shown in Figure 5 are only for one orientation of the species. Thus, we can conclude already from the quantum mechanical calculations that an electrostatic approach to the field gradient on Li^+ in aqueous solution is unrealistic, and that any agreement, better than an order of magnitude with experiment or other refined theories, is purely a coincidence.

It is interesting to note that the SCF curve is very flat in the neighbourhood of the energy minimum. This means that an increase in the Li-O distance from 3.3 to 4.3 a.u. will not cause any appreciable change in the field gradient. However, the field gradient obtained when taking only electrostatic effects into account, will decrease by 2/3 for the same geometry change. Such a difference is of course even more serious when studying the field gradient fluctuation.

5.3 Statistical Mechanical Calculation of the Field Gradient Fluctuation

The results from the various simulations are summarized in Table 4. The last column of that table shows the correlation times calculated with Eq. (8) using an experimental relaxation rate together with the field gradient fluctuation obtained in the corresponding simulation. The value $R = 0.027 \text{ s}^{-1}$, is taken from a work by Hertz [30,16]. The quadrupole moment, Q , was taken to be $-0.04 \cdot 10^{-28} \text{ m}^2$ [31].

The results in Table 4 reveal that the fluctuation is roughly the same in all calculations, and independent of the simulation conditions. When N , the number of water molecules, is increased there is a slight tendency to weaker fluctuations.

The density of the system, i.e. the radius of the MC-"sphere", causes very small effects on the magnitude of the fluctuations. The fluctuation for $N=50$ and $\rho=1.0$ (corresponding to a density of 1 g/cm^3) differs slightly from the other cases. This may be due to an insufficient number of configurations used in that simulation. The large value of the field gradient points towards this possibility. An important conclusion that can be drawn from Table 4, is that the field gradient fluctuation is to a large extent determined by the water molecules in the first shell.

Included in Table 4 is also a calculated value of the correlation time, τ_{eff} , using an experimental relaxation rate. Our calculated correlation time is approximately a factor of three lower than the corresponding quantity for the deuterium quadrupolar relaxation in D_2O [35]. This difference is not unexpected, since there is no obvious reason to assume that the specific motion(s) of the water molecules causing the relaxation of ^7Li should be the same as the motion causing the relaxation of ^2D in D_2O .

The Monte Carlo method enables one to make a rather detailed analysis distinguishing between the contributions from different water molecules. Figure 6 contains six histograms, showing how the field gradient fluctuation varies with the number of water molecules taken into account, beginning with the nearest, the two nearest water molecules etc. (solid lines). The dashed lines show the separate contributions from the nearest, the next nearest water molecule etc. From these histograms several conclusions can be drawn: i) the first hydration shell accounts for the major part of the fluctuation, ii) the individual molecules in the first shell give about the same contribution and iii) the water molecule correlation plays an important role. The last conclusion can be seen from the fact that the total field gradient fluctuation is not equal to the sum of the individual contributions.

5.4 Comparison with Other Models

Deverell [9] suggests that the field gradient fluctuation for the most part is an effect of an overlap between the wave functions of the ion and a colliding water molecule. The overlap distorts the otherwise spherical electron cloud of the ion, giving rise to a field gradient at the nucleus. That Deverell's model is inadequate for at least Li^+ can be seen from the fact that: if it is the colliding molecule that causes the field gradient, one would believe that the contribution from the nearest water molecule should be the largest, and that the next nearest etc. should give negligible contributions. This is contrary to our findings (see Figure 6). In fact, for all Li-O distances in the first shell one obtains approximately the same field gradient at the Li^+ nucleus. This is probably due to a delicate balance of overlap, higher order polarization and electrostatic effects and any theory neglecting for example the electrostatic term will give an unbalanced description.

Hertz [11] has in two articles derived rather elaborate expressions for the relaxation rate of small ions in aqueous solution. In contrast to Deverell, Hertz has focused attention on

the electrostatic contribution to the field gradient fluctuation which he assumes to be the most important. In the model, the field gradient is caused by point dipoles representing the water molecules, either treated individually or as a continuum. The predicted relaxation rates with either of Hertz's models are in surprisingly good agreement with experiment [11]. However, this can in our opinion not be taken as a proof of the validity of Hertz's theory, since the final expressions contain a number of adjustable parameters. This parameter set include the ionic radius, the radius of a water molecule, a polarization factor and a correlation time. The correlation time used is that for pure D_2O , with an uncertain correction factor. As mentioned above, this is questionable since the dynamical features of a bulk water molecule and that of a water close to an ion may be quite different. Since, Hertz also neglects all interactions except the pure electrostatic ones, he will obtain a field gradient function according to the curve (b) in Figure 5, which is at best qualitatively correct.

Friedman [13] has generalized a model, which accounts for the electronic paramagnetic resonance relaxation of the nickel ion in water. He has shown that the field gradient fluctuation obtained in the experiment, can be accounted for by considering the distortion from cubic symmetry, of a $Ni^{2+} + 6H_2O$ complex found in crystals. The distortion is referred to as a "wagging" motion, and is a consequence of the formation of hydrogen bonds with water molecules outside the first shell.

The similarity of the formalisms for the nuclear and electronic quadrupole relaxation, enables Friedman to extend his model to account for the relaxation of quadrupolar nuclei in aqueous solution as well. The predicted relaxation rates, with this model, is in fair agreement with experiments, the largest discrepancy being that for the lithium ion.

Since Friedman, like Hertz, has assumed the electrostatic contribution to be the dominant, his results will be affected by this assumption. However, it may anyway be interesting to see whether the proposed "wagging" of the water molecules can create any substantial field gradient or not. The "wagging" motion consists of a simultaneous change in the Li-O distance and in the water orientation. Since we have already established that a change in the Li-O distance will not cause any significant change in the field gradient, we eliminate that coordinate from further considerations. We have tested Friedman's model by performing a MC simulation, where the oxygen atoms were held fixed and the water molecules were allowed to rotate around the respective oxygen atoms, which were placed octahedrally around the Li^+ ion. This model includes, besides the "wagging" mode suggested by Friedman, also a rotation around the dipole vector, but the fluctuation obtained in such a simulation was only 1/10 of the value found in a simulation without any restrictions.

5.5 Refinement of the Present Model

Several approximations have been made in this calculation. Starting with the quantum mechanical calculations, we have restricted ourselves to work within the Hartree-Fock approximation, and with a limited basis set, although fairly large. The errors introduced hereby in the energy and field gradient functions are presumably small and of negligible importance. The restriction imposed by having a rigid water molecule geometry does not seem to introduce any substantial error [22].

The transformation of the discrete quantum mechanically calculated energies and field gradients to analytical functions, introduces some error, but experience show that this is in general rather small, a few percent [32].

The assumption of pair-wise additivity of the field gradient has been tested in this work and found to be satisfactorily accurate. However, the assumption of a pair-wise additive total

energy is more crucial, since the water molecules, at least in the first shell, become substantially polarized by the Li^+ ion, which of course affects their mutual interaction. Calculations by Clementi et al. [20] show that the inclusion of many-body effects in a $\text{Li}^+(\text{H}_2\text{O})_4$ complex increases the average $\text{Li}^+ - \text{H}_2\text{O}$ interaction by about 20 kJ/mole. However, they do not report how the pair correlation function is affected. Since our calculated $\text{Li}-\text{H}_2\text{O}$ structure agrees surprisingly well with the experimental results obtained by Enderby and Neilson [25] (see Table 3), there is at least some evidence that inclusion of many-body effects will not drastically alter the structure around the Li^+ ion.

The rigid boundary conditions used in this work may be improved by introducing a dielectric continuum outside the sphere, taking account of its polarization in some way. This can, for example, be done with the reaction field technique suggested by Friedman [33].

In summary, we conclude that the largest uncertainty in the present results comes from the neglect of many-body effects in the energy evaluation in the simulations. It is difficult to estimate the error without performing explicit calculations, which become rather time-consuming. The remaining approximations probably introduce smaller errors than do the statistical errors in the simulations.

6. CONCLUSIONS

This work is an example of how the Monte Carlo simulation technique can be used as a tool to facilitate the interpretation of experimental data. A NMR study of ^7Li quadrupolar relaxation in dilute aqueous solution gives a product of two unknown quantities, an electric field gradient fluctuation and a correlation time respectively, the former being accessible from Monte Carlo simulations.

Both in the energy and field gradient calculations the approximation of pair-wise additivity was supposed to hold. This

approximation seems to be fairly accurate for the field gradient, while the consequences for the energy are harder to estimate.

The field gradient at the Li^+ nucleus arising from a water molecule close to it, was shown to consist not only of purely electrostatic contributions, but large contributions from overlap and higher order polarization effects as well.

The field gradient fluctuation at the Li^+ nucleus was found to be quite insensitive to different simulation conditions, like the density of the system and the number of water molecules, provided there are enough to fill the first shell. These findings imply that the nearest water molecules, i.e. the first hydration shell, give the dominating contribution to the fluctuation.

A closer look at the contributions from individual molecules in the first shell, revealed that they could give rise to field gradient fluctuation of the same order of magnitude as the total value from all water molecules. However, the individual contributions largely cancel when summed up, due to the correlated motion of the water molecules.

The first hydration shell was found to have an average hydration number just above five, which implies a non-cubic average arrangement of the water oxygens. In general, it was found that irrespective of the momentaneous hydration number (4,5 or 6), the resulting field gradient fluctuation was roughly the same. It was also found that the main contribution to the fluctuation originated from a lateral rather than a radial deformation of first hydration shell.

The evaluated field gradient fluctuations give the opportunity to calculate an effective correlation time from experimental data. The correlation time was found to be approximately 1 picosecond. It is not possible to extract more detailed dynamical information,

and the nature of the motion or motions responsible for the relaxation, can possibly be determined only by performing Molecular Dynamics simulations.

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 Distance 1 a.u. = 0.529167 10E-10 m
 Energy 1 a.u. = 4.3591 10E-18 J
 Field Gradient 1 a.u. = 9.7175 10E+21 V/m**2
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TABLE 1. Parameter values obtained in the fitting procedures of energies and field gradients to Eqs. (14) and (18) respectively (atomic units [34]).

Parameter	Oxygen (O)	Hydrogen (H)
<u>Energy:</u>		
Q	-0.6270	0.3135
A	-0.598	0.171
B	53.151	1.049
C	-1568.15	-1.869
<u>Field Gradient:</u>		
D	-1.421	0.546
E	-5.217	0.211
F	24.446	0.638

TABLE 2. Electric field gradient at the Li^+ nucleus and interaction energy ΔE for various configurations (see Fig. 3) of the system $\text{Li}^+ + 2\text{H}_2\text{O}$. Field gradients obtained with the pair-approximation, Eq. (17), are given in parenthesis (atomic units [34]).

Configuration	$\Delta E/\text{kT}$	$V_{xx} \cdot 10^4$	$V_{yy} \cdot 10^4$	$V_{zz} \cdot 10^4$	$V_{yz} \cdot 10^4$
a	-106.8	(72 74)	-137 -137	65 63	0 0)
b	-109.1	(70 74)	158 163	-228 -237	0 0)
c	-94.5	(155 162)	-102 -81	-53 -81	0 0)
d	-106.0	(158 163)	-161 -159	3 -4	0 0)
e	-99.1	(112 118)	-77 -59	-35 -59	20 59)
f	-76.5	(44 40)	90 84	-134 -124	0 0)

TABLE 3. Hydration of ions in aqueous solution obtained from X-ray, neutron diffraction and Monte Carlo simulations.

Solute	Concentration (m=molal, N=normal)	Li ⁺ -Oxygen distance (Å)	Li ⁺ -Deuterium distance (Å)	Hydration number
<u>Experiments:</u>				
LiBr (a)	2.1 N	2.25	-	4-6
Li ₂ SO ₄ (b)	2.22 m	2.08	-	4
LiCl (c)	6.9 m	1.95	-	4±1
LiCl (d)	3.57 m	1.95±0.02	2.55±0.02	5.5±0.3
<u>Present Work:</u>				
Li ⁺ + 6H ₂ O		1.99±0.02	2.65±0.02	5.1±0.3
Li ⁺ + 50H ₂ O		2.01±0.02	2.68±0.02	5.3±0.4
Li ⁺ + 150H ₂ O		2.02±0.03	2.67±0.04	5.5±0.5

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(d) Reference [25b].

TABLE 4. Results from Monte Carlo simulations. N = number of water molecules, kconf = number of configurations (in thousands), ρ = density of the system. $\langle V_{zz} \rangle$ and $\langle V_{zz}^2 \rangle$ are the field gradient and its fluctuation, and the values in parenthesis are their rms deviations. $\tau_{\text{eff}} =$ the effective correlation time calculated with Eq. (8). (atomic units [34])

N	kconf	ρ (g/cm ³)	$\langle V_{zz} \rangle \cdot 10^4$	$\langle V_{zz}^2 \rangle \cdot 10^4$	$\tau_{\text{eff}} \cdot 10^{12}$ (s)
6	500	1.11	-1 (10) †	0.14 (0.02)	1.1
6	400	0.91	-3 (10)	0.15 (0.03)	1.0
6	400	0.05	0 (10)	0.17 (0.03)	0.9
50	400	1.00	32 (15)	0.19 (0.06)	0.8
50	1200	0.91	-4 (15)	0.14 (0.05)	1.1
50	625	0.37	9 (15)	0.14 (0.04)	1.1
150	1050	0.91	-4 (15)	0.11 (0.05)	1.4

† The rms (root mean square) deviation is calculated from subaverages taken over 20,000 configurations.

Figure captions:

Figure 1. The total potential energy, $\langle U \rangle$, versus the number of configurations (in thousands), KCONF, generated in the MC-simulation of $\text{Li}^+ + 150 \text{ H}_2\text{O}$. The calculation is divided in two parts and the averages are calculated during the second part (Analyses).

Figure 2. Definition of distances and angles introduced in Eqs. (14) and (18). θ_1 can be anyone of the angles Z-Li-O, Z-Li-H1, Z-Li-H2 or O-Li-O.

Figure 3. Geometries used in the study of the field gradient at the Li^+ nucleus in the system $\text{Li}^+ + 2\text{H}_2\text{O}$. In all geometries the water dipole vectors coincide with respective Li-O vectors. The Li-O distances are in all cases 1.88 Å, except for configuration f, where they are 1.88 Å and 4.76 Å respectively. > denotes that the water molecule is in the YZ-plane, and ► that it is perpendicular to it.

Figure 4. The distribution of O-Li-O angles in the first hydration shell ($\text{Li}^+ + 150 \text{ H}_2\text{O}$). a) Total averages with a mean hydration number of 5.5 b) Subaverage when the mean hydration number was 6.

Figure 5. The field gradient at the Li^+ nucleus caused by:

a) a water molecule in the system $\text{Li}^+ \dots \text{O} \begin{array}{l} \nearrow \text{H} \\ \searrow \text{H} \end{array}$,

determined with ab initio SCF calculations at various Li-O distances. (atomic units [34])

b) an ideal dipole, radially oriented, and with its field gradient multiplied by $(1 + \gamma)$.

Figure 6. The field gradient fluctuation from the nearest, the two nearest water molecules etc. relative to the Li^+ ion (solid lines), and the separate contribution from the nearest, the next nearest water molecule etc. (dashed lines), for different simulations: A) $\text{Li}^+ + 6 \text{ H}_2\text{O}$, B) $\text{Li}^+ + 50 \text{ H}_2\text{O}$ and C) $\text{Li}^+ + 150 \text{ H}_2\text{O}$. (atomic units [34]).

Fig 1

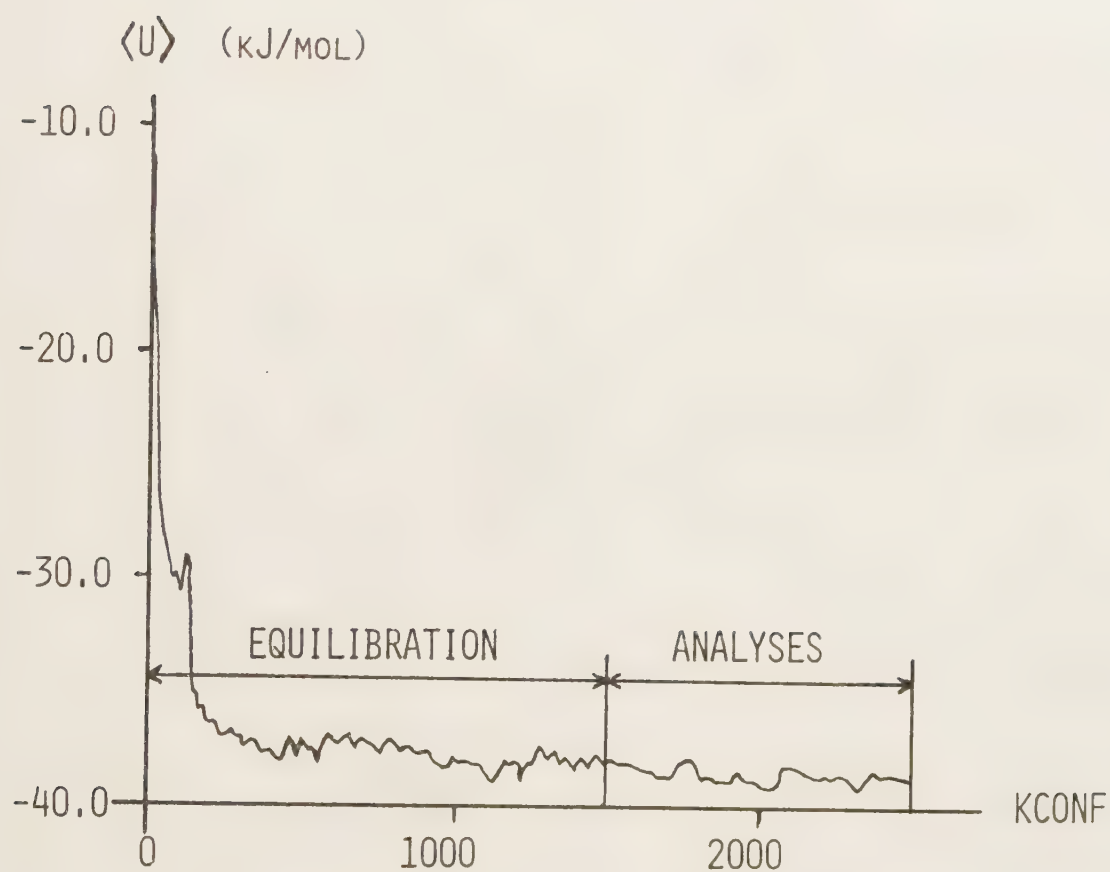


Fig 2

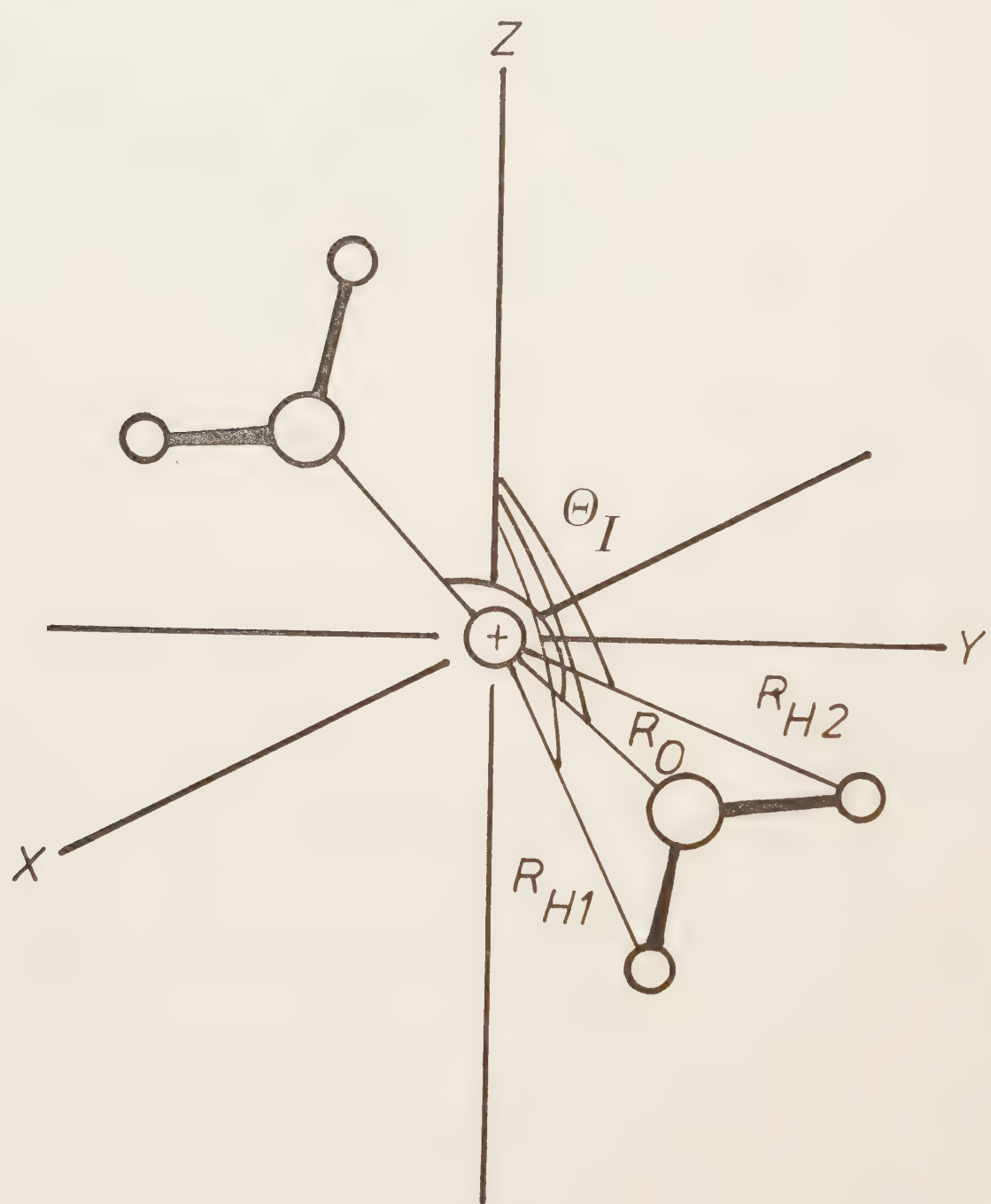


Fig 3

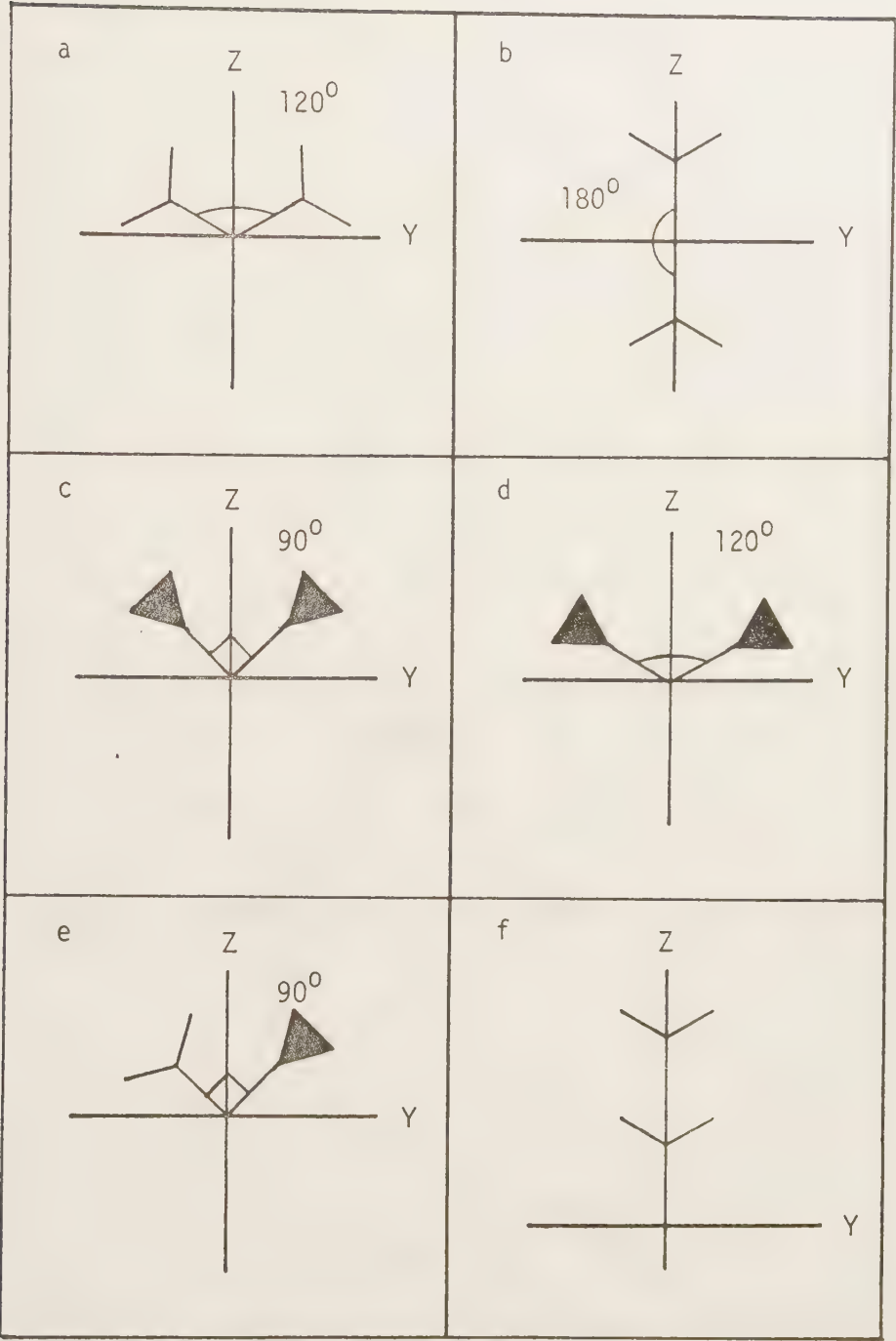


Fig 4

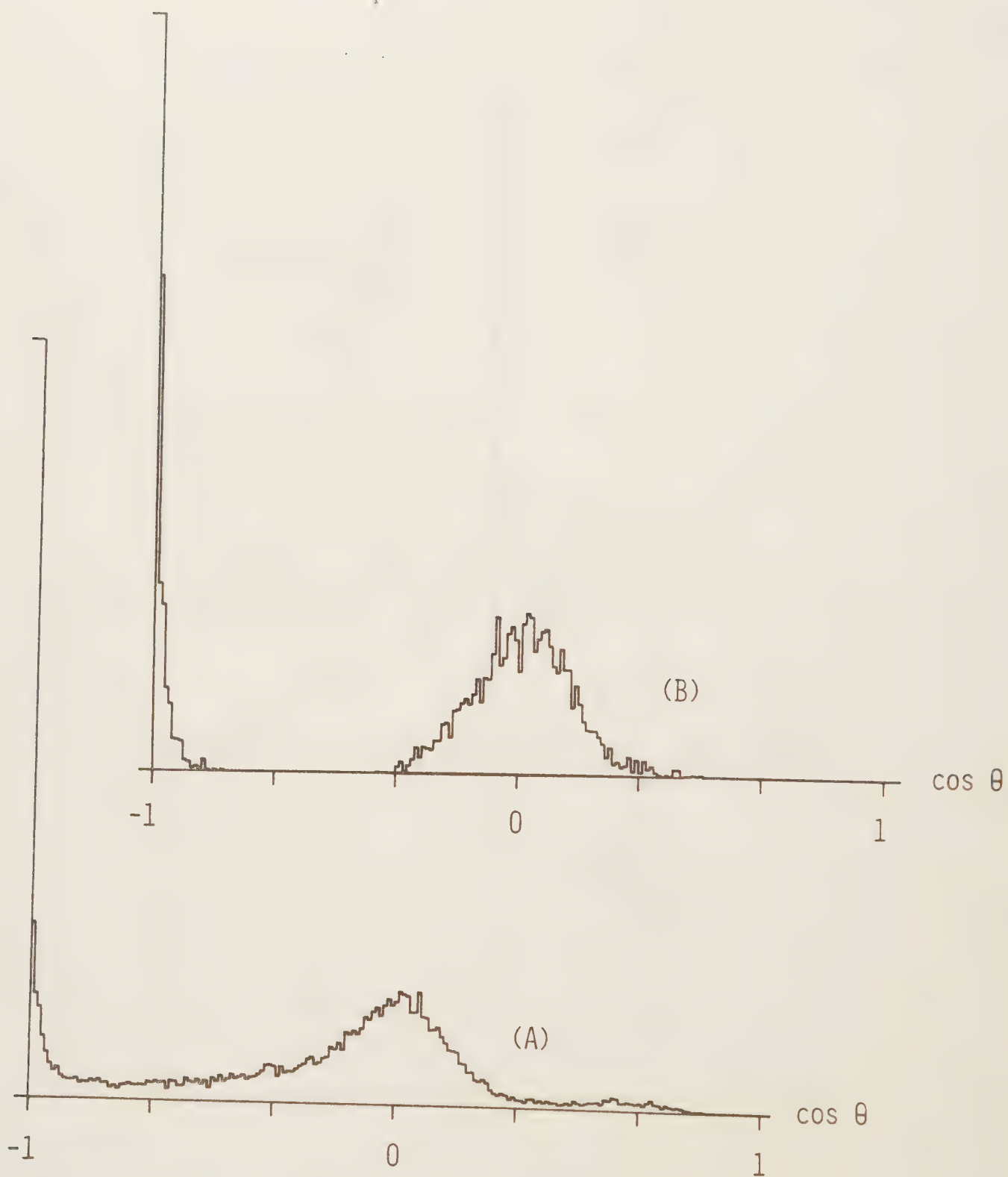


Fig 5

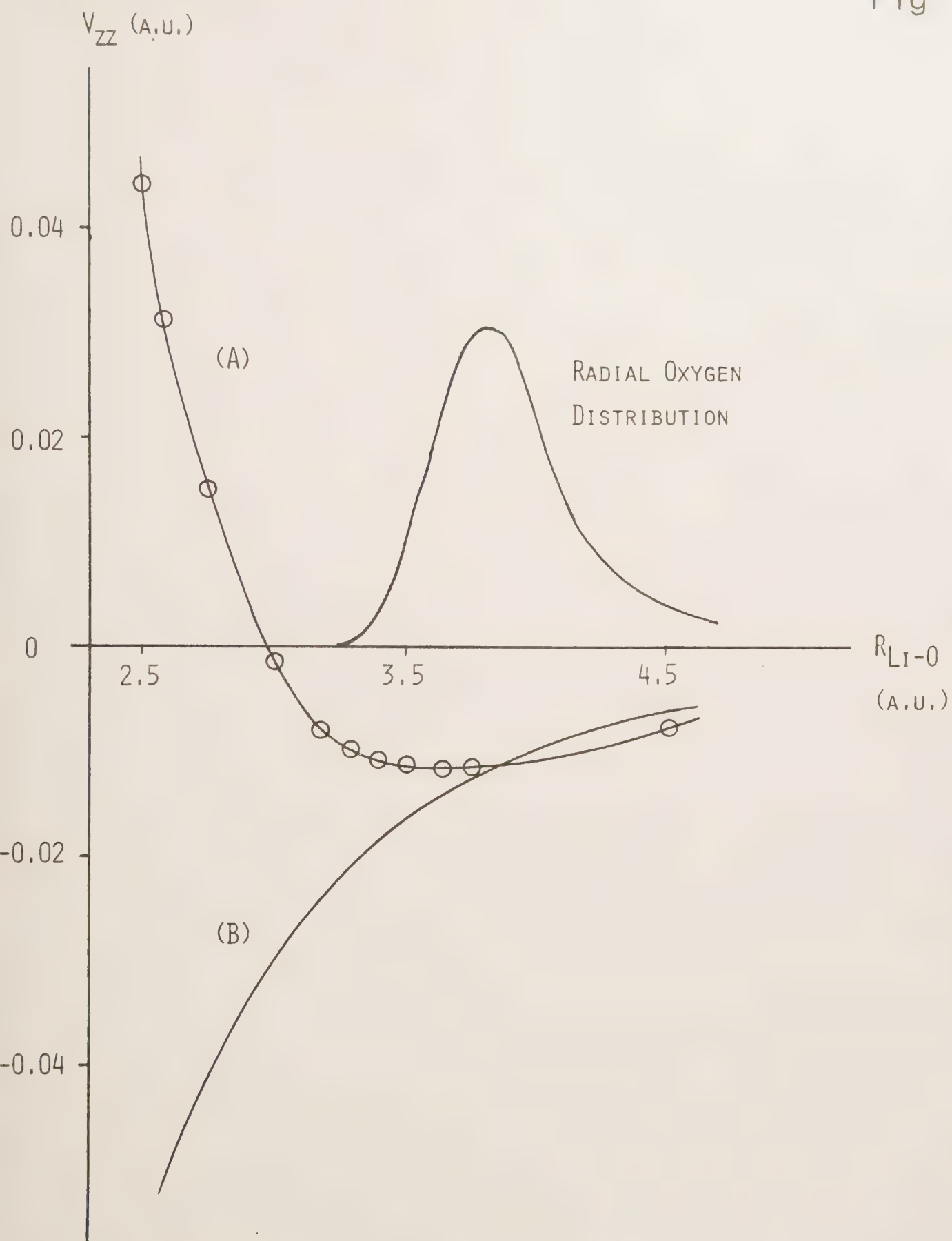
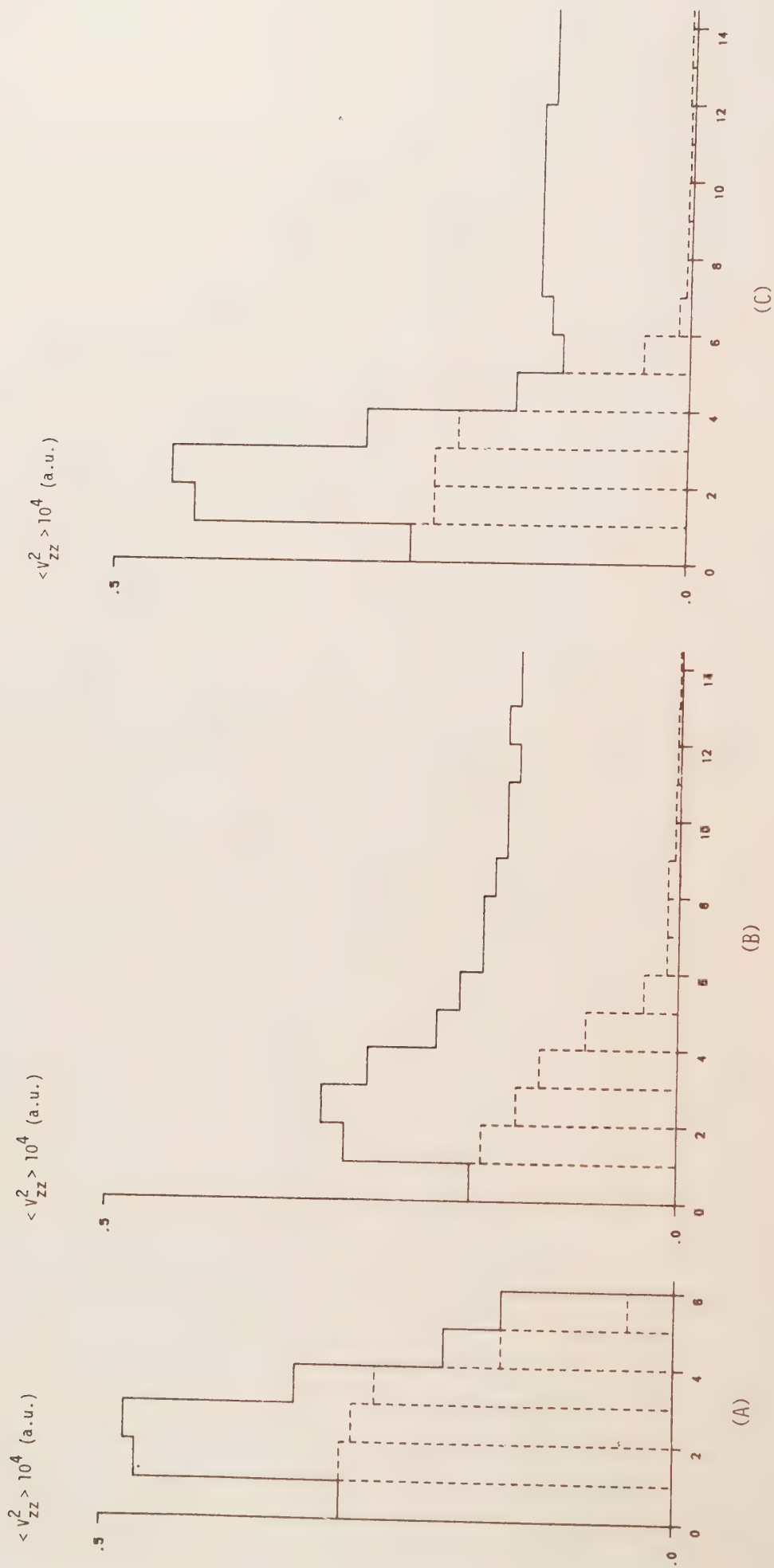


Fig 6



NUMBER OF WATER MOLECULES

Ion Condensation on Planar Surfaces. A Solution of the Poisson–Boltzmann Equation for Two Parallel Charged Plates

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The Poisson–Boltzmann equation is solved analytically for the case of two parallel plates with an intervening aqueous solution containing only counterions. This is the situation one has in lamellar liquid crystals. Different aspects of the counterion distribution are considered, and a number of invariance properties are found. At large distances between the plates the counterion concentration remains constant far from the plates, as the surface charge density is varied. The counterion concentration close to the surface remains constant as the distance between the plates is varied at constant surface charge density. In the limit of an infinite distance between the plates and a reasonably high surface charge density, the counterion distribution is unaffected by salt addition at distances from the surface that are small compared to the Debye length. Finally, the counterion distribution is independent of temperature. Similar invariances are well known for solutions of rod-shaped polyions, where the behavior has been termed counterion condensation. It appears that the present treatment reveals fundamental and simple properties of the counterion distribution outside planar charged surfaces that should be of importance for the understanding of a number of chemical processes outside such surfaces, including biological systems.

1. Introduction

Charged surfaces immersed in (aqueous) electrolyte solutions are of importance not only in electrochemical reactions, but also in certain systems of amphiphilic molecules, such as lamellar liquid crystals and biological membranes. The ion distribution in the solution outside

such a charged surface is of great importance for the chemical behavior of the system. This ion distribution is, in an electrostatic continuum model, described by the Poisson–Boltzmann equation (SI units)

$$\epsilon_r \epsilon_0 \nabla^2 \Phi = -\rho = -\sum_i n_i \exp(-z_i e \Phi / kT) \quad (1)$$

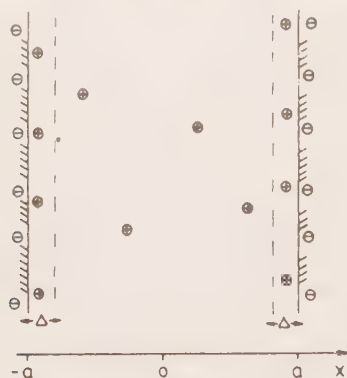


Figure 1. Schematic representation of two parallel charged plates with only counterions in the intervening solution. The distance between the plates is $2a$.

where the sum on the right-hand side extends over all types of ions in the solution. The electrostatic potential is denoted Φ , ϵ_0 is the permittivity of a vacuum, ϵ_r the relative permittivity, ρ the charge density, n_i is a normalization constant with the dimension of a charge density, $z_i e$ is the charge of the ion i , k is Boltzmann's constant, and T is the absolute temperature.

Nearly all theoretical treatments of electrolyte solutions are based on the Poisson-Boltzmann equation, and its solutions have been extensively studied for a number of cases. The ion distribution outside a planar surface was first studied independently by Gouy¹ and Chapman² and their theory has provided the basis for, among other things, discussion of the stability of colloids³ and of the ion distribution outside charged biological membranes.⁴

In the present paper we present an analytical solution of eq 1 for the simple case of two parallel charged planar surfaces with an intervening solution containing only counterions (see Figure 1). These are just the conditions one has in a lamellar phase of a lyotropic liquid crystal⁵ and the calculation was originally performed to obtain an understanding of experimentally observed NMR quadrupole splittings for the counterions in such systems.⁶ However, it will be shown that the calculations have important implications over a wider context.

2. Solution of the Poisson-Boltzmann Equation

For the situation depicted in Figure 1, eq 1 is simplified to

$$d^2\Phi/dx^2 = -(n/\epsilon_r\epsilon_0) \exp(-ze\Phi/kT) \quad (2)$$

The boundary conditions are, by symmetry

$$\left. \frac{d\Phi}{dx} \right|_{x=0} = 0 \quad (3)$$

and through electroneutrality

$$\left. \frac{d\Phi}{dx} \right|_{x=a} = -\left. \frac{d\Phi}{dx} \right|_{x=-a} = \sigma/\epsilon_r\epsilon_0 \quad (4)$$

Here σ is the surface charge density of the plate. Equation 2 can be integrated in the standard way⁷ using the identity

$$2 \frac{d^2\Phi}{dx^2} \frac{d\Phi}{dx} = \frac{d}{dx} \left(\frac{d\Phi}{dx} \right)^2 \quad (5)$$

The integration results in

$$\frac{d\Phi}{dx} = \pm (2nkT/\epsilon_r\epsilon_0 ze)^{1/2} [\exp(-ze\Phi/kT) - 1]^{1/2} \quad (6)$$

In eq 6 the potential at $x = 0$ has been chosen equal to zero, i.e. $\Phi(0) = 0$, since the absolute value of the potential is

arbitrary. For a negatively charged surface as in Figure 1 the plus sign in eq 6 refers to the range $0 \leq x < a$, and the minus sign refers to the range $0 \geq x > -a$. Equation 6 can also be integrated analytically, and the solution is, for $0 \leq x < a$

$$\Phi(x) = -(kT/ze) \ln \{ \tan^2(sx/a) + 1 \} = (2kT/ze) \ln \{ \cos(sx/a) \} \quad (7)$$

$$d\Phi(x)/dx = -(2kTs/zea) \tan(sx/a) \quad (8)$$

$$d^2\Phi(x)/dx^2 = -(2kTs^2/zea^2) \{ \tan^2(sx/a) + 1 \} = -(2kTs^2/zea^2) / \cos^2(sx/a) \quad (9)$$

where the dimensionless parameter s is given by

$$s \equiv (nze/2kT\epsilon_r\epsilon_0)^{1/2} a \quad (10)$$

For $-a < x \leq 0$ $\Phi(x)$ and $d^2\Phi(x)/dx^2$ are unchanged, while $d\Phi(x)/dx$ changes sign. The boundary condition eq 4 provides an equation for the parameter s

$$s \tan(s) = (-\sigma)zea/(2kT\epsilon_r\epsilon_0) \equiv K \quad (11)$$

The solution, eq 7-9, is different from the corresponding Gouy-Chapman solution for a single plate, in that the former involves trigonometric rather than exponential functions. The consequences of eq 7-11 can be analyzed in a number of ways. It is then a considerable help to refer to the theory of polyelectrolyte solutions, which has been more completely analyzed.

3. Ion Condensation on the Charged Surface

Polyelectrolyte solutions have several properties that make them qualitatively different from normal electrolyte solutions. The basic reason for this is that the polyelectrolyte has a larger charge, which often makes the absolute value of the electrical potential, in the vicinity of the polyion, large compared to kT/ze . Due to the high potential, part of the counterions will reside in the vicinity of the polyion while others, further away from the polyion, will move more or less freely.

Particularly for rod-shaped polyions the counterion distribution has been rather thoroughly investigated.^{8,9} In the absence of added salt it is possible to solve eq 1 analytically for an infinite rod.^{10,11} When salt is present it is necessary to solve the equation numerically,^{12,13} or to use approximate analytical solutions.¹⁴ Of the various results obtained in these and other calculations^{8,9} on rod-shaped polyions, we list three general conclusions that are of importance for the analysis of the situation with planar surfaces:

(i) When the charge density on the polyion is increased above the critical value one unit charge per $e^2/(4\pi\epsilon_r\epsilon_0 kT)$ of length (SI units) all added counterions reside close to the polyion, and the counterion concentration far from the polyion remains constant.

(ii) As the polyion concentration is decreased the fraction of ions bound to the polyion remains constant.

(iii) Addition of a simple electrolyte to a polyion solution does not change the number of bound ions.

This behavior of counterion distribution above the critical charge density has been termed ion condensation⁸ on the polyion.

Outside a planar charged surface the electrical potential can also be large compared to kT/ze , and one would expect the counterion distribution to have somewhat similar properties to those found for rod-shaped polyions. An analysis of the solution of eq 1 in eq 7-9 reveal that in fact all the three properties of solutions of rod-shaped polyions listed above are also shown by the counterion distribution outside a planar surface.

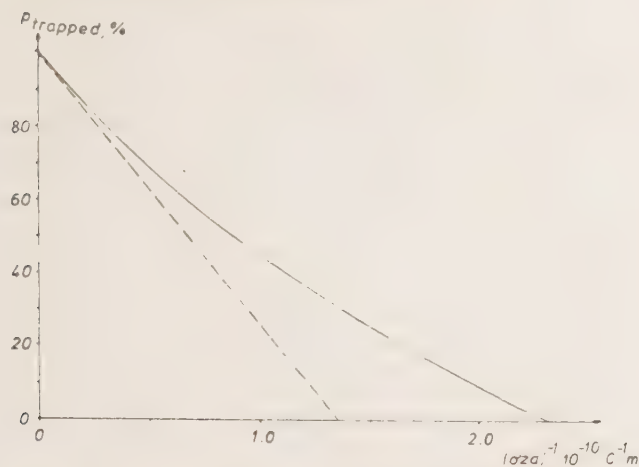


Figure 2. The fraction of trapped ions according to eq 13 plotted vs. $-(\sigma za)^{-1}$. The straight line is obtained by extrapolating the initial slope.

In eq 11 the parameter s can have values in the range $0 \leq s < \pi/2$. When K is much larger than unity s approaches $\pi/2$ and in this range s will vary only very little when the surface charge density σ is changed. The counterion concentration is according to eq 1 given by the second derivative of the potential in eq 9 times $\epsilon_r \epsilon_0$. At a point x_f not close to the surface $\cos(sx_f/a)$ varies only moderately with a small change in s , and the charge density $\rho(x_f)$ varies only little as σ is changed at high values of σa .

When discussing the distribution of the ions interacting strongly with the charged surface, one has to distinguish between those ions that are in direct contact with the surface and those that are trapped by the electrical potential, but, on a molecular scale, are well separated from the ions on the surface. The distinction between trapped and free counterions is only conventional, and we chose to define ions as trapped when the potential exceeds $-kT/ze$. The fraction, p , of ions within a distance δ from the charged surface is obtained directly from the difference in the electric field at $x = a$ and $x = a - \delta$. Thus

$$p = 1 + \{2\epsilon_r \epsilon_0 kTs / (\sigma zea)\} \tan(s - s\delta/a) \quad (12)$$

When δ is chosen to make $\Phi = -kT/ze$ the fraction p becomes

$$p_{\text{trapped}} = 1 + 2.62\epsilon_r \epsilon_0 kTs / (\sigma zea) \quad (13)$$

In Figure 2 p_{trapped} is plotted vs. $-(\sigma za)^{-1}$. This dependence is very similar to $p_{\text{trapped}} = 1 - \sigma_{\text{crit}}/\sigma$ found for rod-shaped polyions. From the linear part of the curve one can extract a critical value of (σza) of

$$-(\sigma za)_{\text{crit}} = 1.31\pi\epsilon_r \epsilon_0 kT/e \quad (14)$$

corresponding to one unit charge per $ae^2/(1.31\pi\epsilon_r \epsilon_0 kT)$ of area, which is in resemblance with the critical line charge density for rod-shaped polyions.

In contrast to macroscopic thermodynamic measurements, spectroscopic parameters of the counterions are only different from those of the bulk solution for those ions that are in direct contact with the charged surface. In this case one is interested in the amount of counterions close to the surface whatever the value of the potential. A first approximation to this quantity is obtained from the counterion charge density ρ_s at the surface. From eq 1, 9, and 11 one has

$$\rho_s = \{2\epsilon_r \epsilon_0 kTs^2 / (zea^2)\} \{(\sigma zea)^2 / (2kT\epsilon_r \epsilon_0 s)^2 + 1\} \quad (15)$$

In the limit when σa is large, eq 15 reduces to

$$\rho_s = \sigma^2 z e / (2kT\epsilon_r \epsilon_0) \quad (16)$$

which shows that in this limit the surface ion concentration

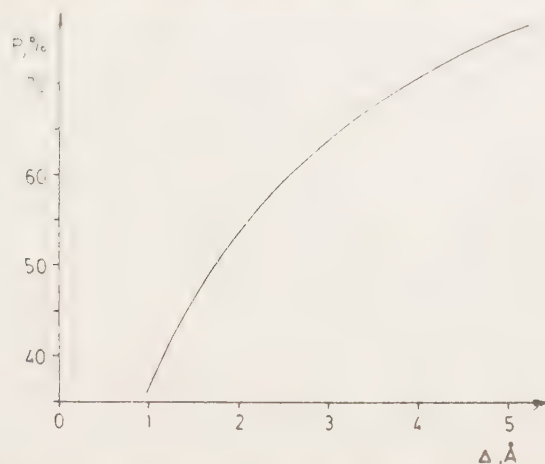


Figure 3. The fraction of contact bound ions vs. the distance Δ : $\sigma = 0.2 \text{ C m}^{-2}$ and $a = 10 \text{ Å}$.

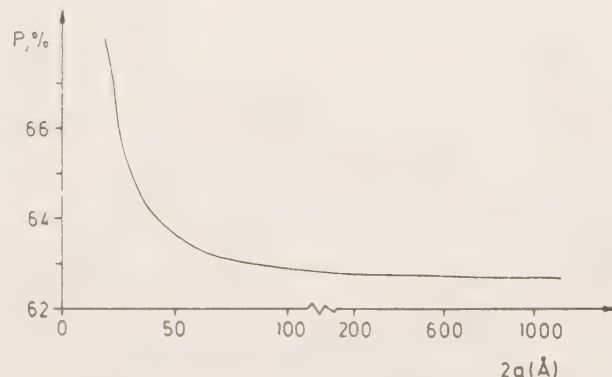


Figure 4. The fraction of contact bound ions vs. the distance between the plates $2a$: $\sigma = 0.2 \text{ C m}^{-2}$ and $\Delta = 3 \text{ Å}$.

is independent of the distance between the plates. This might be a surprising result but in the limit of large σa , the potential at the surface is

$$\Phi(a) = -2kT/(ze) \ln \{ \sigma zea / (\pi kT\epsilon_r \epsilon_0) \} \quad (17)$$

and the constant ion concentration at the surface is maintained on dilution since the entropic factor that tends to decrease ρ_s is exactly cancelled by an increase in the potential, as is seen in eq 17.

For many values of σ the value of ρ_s is unreasonably high. This is caused by the fact that in the purely electrostatic treatment, the molecular nature of the ions has been neglected. To obtain an estimate of the fraction of ions bound to the surface, one has to integrate the charge density a distance Δ (cf. Figure 1) out from the surface, where Δ should be of the order of a counterion diameter, possibly including its hydration sheath. From eq 11 and 12 the fraction of contact ions p_c can be calculated. Figure 3 shows that p_c does not vary dramatically when reasonable values of Δ are chosen. The integrated charge density measured by p_c also does not depend on the distance a at constant σ for large values of σa , as shown in Figure 4. In this sense the fraction of contact bound ions behave differently from the fraction of trapped ions which increases as a increases (cf. Figure 2). In the limit $a \rightarrow \infty$ eq 12 reduces to

$$p_c = 1 - \{1 - \Delta \sigma z e / (2\epsilon_r \epsilon_0 kT)\}^{-1} \quad (18)$$

using eq 11 and standard trigonometric relations. This corresponds to the asymptotic value in Figure 4.

When a simple electrolyte is also present in the solution between the charged plates, eq 1 has a solution only in terms of an elliptical integral,³ and it is not straightforward

to investigate how the addition of salt influences the counterion distribution. However, for the limiting case when the distance between the plates is infinite, the Gouy-Chapman^{1,2,6} equations apply. In the limit when the potential at the surface is high compared to kT/ze , i.e., when $\sigma/c^{1/2} > 0.1$, where c is the concentration of the 1:1 electrolyte, one finds that the concentration of counterions, ρ_s , at the surface is independent of the electrolyte solution and given by eq 16. Furthermore, when the Debye length $\kappa^{-1} = (2ze^2c/(\epsilon_r\epsilon_0kT))^{-1/2}$ is long compared to the distance Δ , the fraction of contact bound ions is given by eq 18. Thus the integrated charge density is also independent of the electrolyte concentration.

4. Ion Condensation in Lyotropic Liquid Crystals

In mixtures of water and surfactant molecules lamellar phases are often formed, particularly when a third weakly polar compound is also present.⁵ For ionic surfactants, these phases are composed of lamellae of hydrophobic moieties alternating with aqueous lamellae containing the counterions. The two types of lamellae are divided by an interface consisting of the polar groups of the surfactant. The calculations presented above should be directly applicable to these types of systems containing ionic amphiphiles.

To obtain numerical values for the constants let us, for example, consider the lamellar phase formed in the system $\text{H}_2\text{O}-\text{Na}^+\text{C}_8\text{H}_{17}\text{OSO}_3^--\text{C}_{10}\text{H}_{21}\text{OH}$.¹⁵ In this case the area per molecule is known from X-ray diffraction studies.¹⁵ In the region of the lamellar phase, where one has so-called one-dimensional swelling, the only structural parameter that changes in the system when water is added is the thickness of the water lamellae. This thickness ($= 2a$) then varies from 20 to 85 Å, and the values of σ is one unit charge per 82 Å². With these values of σ , $2a$ determined at 20 °C and standard values for the other parameters in eq 11, the constant K is substantially larger than unity and the parameter s is close to $\pi/2$.

In Figure 4 the parameters have been chosen in accordance with these values. It follows that the number of ions in contact with the charged surface is approximately concentration independent. A further significant consequence is that the counterion distribution is approximately temperature independent in aqueous solutions. This comes about since ϵ_r is roughly inversely proportional to T . In all the equations for the counterion distribution ϵ_r and T enters as a product and their temperature dependencies cancel, whereas from a superficial look at eq 1 one would expect an exponential dependence on T for the ion distribution! It is also gratifying to note that the fraction of bound ions predicted from eq 18 is of the same order of magnitude as those derived from experiments ($p_b \approx 0.4-0.5$).⁵ The properties of the ion distribution in liquid crystals predicted above will be discussed in an independent paper¹⁶ dealing with nuclear magnetic resonance investigations on the counterions.⁶

5. Conclusions

It has been shown that the counterion distribution outside charged planar surfaces has properties very similar

to those previously found in solutions of rod-shaped polyelectrolytes. Thus the counterion concentration far from the surface is independent of the surface charge density σ when $\sigma a > (\sigma a)_{\text{crit}}$ of eq 14. In this region all the added counterions are trapped if $ze\Phi/kT < -1$, as shown by Figure 2. When the distance between the plates is made sufficiently large the number of ions in close contact with the charged surface remains constant, according to eq 16 and 18.

That salt in reasonable concentrations does not influence the counterion distribution is shown by the fact that eq 16 and 18 can also be derived from the Gouy-Chapman solution of eq 1 for a single planar charged surface in an electrolyte solution. It thus seems that the three characteristic properties of a polyelectrolyte solution listed in section 3 also apply to the ion distribution outside planar surfaces.

Similar properties of the ion distribution outside model membranes have been derived by McLaughlin et al.,¹⁷ using the Gouy-Chapman theory. Specifically they find that the number of bound divalent ions is independent of the concentration over a certain interval. Furthermore, McLaughlin et al. show that the simple theory is in excellent agreement with experimental measurements of the surface potential. It is also clear from this paper that the counterion distribution outside a charged membrane is of high biological relevance. In their monograph on colloid stability,³ Verwey and Overbeek discuss the counterion distribution outside a charged surface, but their presentation does not reveal the simple regularities discussed above. Finally, it appears from an analysis of a variety of experimental data that an ion condensation type behavior is also found in micellar solutions.^{18,19}

Acknowledgment. Illuminating discussions with Gilbert Weill and Björn Lindman are gratefully acknowledged.

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v

Alkali Counterion Binding Specificity in Lamellar Liquid Crystals

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The competition between alkali cations for ion binding in a lyotropic lamellar liquid crystal has been determined by measuring the NMR quadrupole splittings of the ionic nuclei. The lamellar phase is formed by the ternary system



when (Y,Z) are (Li,Na), (Li,K), (Li,Cs), (Na,K), (Na,Cs), and (K,Cs). The quadrupole splittings are measured for 7Li , ^{23}Na , and ^{133}Cs as a function of the relative amount of the ions Y and Z. The measurements show that when the splitting for one ion increases, the splitting of the second decreases. Thus one has a true competitive behavior with the affinity sequence $Li^+ > Na^+$, $Cs^+ > K^+$. Attempts are made to interpret the data using three different models based on the Poisson-Boltzmann equation. The first model introduces the ion specificity by assuming distances of closest approach to the lamellar surface for the competing ions. This treatment gives only a moderately good agreement with the experiments. With the other two models it is shown that the experimental data are accurately described by either allowing the ions to bind to sites at the surface, or by assuming an extra potential for an ion in a region close to the surface.

INTRODUCTION

Electrostatic interactions play an important role in determining structure and energetics in aqueous systems containing colloidal particles, not least in biological systems. Macromolecules and colloidal aggregates that carry a high formal charge will attract counterions with the formation of a so-called double layer. Without the screening effects of the counterions the interactions between the macromolecules would be overwhelmingly large, and it is clear that any consideration of interaction energies must include the effect of the ions in the aqueous medium. The standard way of treating the electrostatic effects is to assume the validity of the Poisson-Boltzmann (PB) equation and determine the free energies associated with the electrostatic interactions from solutions of this equation. A classical example of this procedure is the work of Verwey and Overbeek on the stability of lyophobic colloids. (1).

Within the framework of the Poisson-Boltzmann equation an ion is characterized mainly by its charge and, of lesser importance, its ionic radius. For ions far, on a molecular scale, from the polyion the only nonnegligible polyion-ion interaction is most probably the ~~Coulomb~~ *Coulomb* interaction, but as the small ion approaches the polyion, it seems conceivable that more short-range forces become important. The question then arises as to whether these short-range effects influence the properties of the ion distribution and which features of the ions determine their specificity?

In both living and model systems the most abundant positive ions are the alkali ions. Only in exceptional cases, e.g., with crown ethers and valinomycin, do these cations take part in a strongly specific complex formation, while in the majority of cases the properties of a polyelectrolyte system do not change dramatically when the cation is altered from Li^+ to Na^+ to K^+ to Rb^+ to

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Cs⁺. However, even in these systems there is a variation in the affinity of the different alkali cations. Such affinity series have been extensively studied, and of the 120 possible sequences only a limited number are actually observed, the most common ones being the lyotropic series Cs⁺ > Rb⁺ > K⁺ > Na⁺ > Li⁺ and the antilyotropic, where the order is completely reversed (2).

In the study of basic physicochemical properties of aqueous colloidal systems the lyotropic liquid crystals, formed by amphiphiles and water, can often be used as model systems. They are thermodynamically stable, and for several systems the basic properties, such as the phase diagram and the dimensions of the aggregates, have been thoroughly investigated (3). In studying the ion-binding properties nuclear magnetic resonance (NMR), directly monitoring the signal of the counterion has provided interesting information (4). For example, it was recently shown (5) that a number of simple properties of the ion distribution that could be derived from a solution of the PB equation (6) actually gave a simple rationalization of large amounts of accumulated experimental NMR data on ion quadrupole splittings.

In the present article we report experimental determinations of NMR quadrupole splittings in lamellar liquid crystalline phases of the ternary systems C₇COOY–C₇COOZ–C₁₀OH–D₂O, where C_n denotes a saturated alkyl chain of *n* carbon atoms, and Y and Z are alkali counterions Li⁺, Na⁺, K⁺, or Cs⁺. The proportions of the counterions Y and Z are varied to obtain a description of the competition between the ions that is as complete as possible. When possible, NMR signals of both ions were recorded. The experimental data are compared with theoretical calculations, using three different models based on the PB equation, with corrections for the short-range interactions between the lamellas and the ions. In two models this specific interaction is introduced through a distance dependent square-

well potential for each type of ion. In the third model the specificity is described in terms of a site-binding at the lamellar surface.

EXPERIMENTAL

Sodium *n*-octanoate, *n*-octanoic acid, and *n*-decanol were purchased from BDH, United Kingdom. Lithium, potassium, and cesium *n*-octanoate were prepared as described in Ref. (7). Samples were prepared by weighing a total amount of ca. 1 g of the chemicals into tubes, that were immediately sealed off. The samples were equilibrated by heating to an isotropic liquid (ca. 150°C), shaking thoroughly, cooling to room temperature, and storing for at least one week at 25°C. The phase homogeneity of the samples was checked by measuring the ²H NMR signal of the heavy water. ²H, ⁷Li, and ¹³¹Cs NMR were performed on a Varian XL-100 spectrometer and ²³Na on a home-built spectrometer equipped with a superconducting magnet (6T) from Oxford Instruments. Both spectrometers are working in the Fourier transform mode. The temperature was 28 and 24°C, respectively. This temperature difference is insignificant for the determination of the quadrupolar splittings.

Ion Quadrupole Splittings

All the alkali ions have abundant isotopes with spin quantum numbers *I* > 1/2 and thus possess quadrupole moments. The lamellar liquid crystal is macroscopically anisotropic and, as the quadrupole interaction does not average to zero, a quadrupole splitting, Δ, occurs in the spectrum. The ions diffuse fast in the system so that the observed Δ is due to an average of the splittings, Δ_{*i*} over all the ionic sites *i* and therefore (8)

$$\Delta = \left| \sum_i p_i \Delta_i \right| \quad (1)$$

where *p_i* is the fraction of ions in site *i*. Close to the interface between the aqueous and apolar lamellae the anisotropy is largest so

that the sum in Eq. [1] will be dominated by sites in this region. At high water contents the experimental data show that the splittings can be interpreted in terms of a single "bound" site, while at lower water contents several sites seem to occur (9). In the case of a single "bound" site the observed quadrupole splitting can be interpreted as proportional to the fraction of "bound" ions. By measuring Δ as a function of the relative amount of two counterions, one can then determine how these ions compete due to the short-range interactions with the charged amphiphilic surface. It is a great advantage to be able to study the signal of both ionic species to check the consistency of the interpretation. If there is an increase in Δ_Y there should be a decrease in Δ_Z .

Theoretical Models

In order to search for a quantitative interpretation of the ion selectivity, three different models have been used within the framework of the Poisson-Boltzmann equation. In the case of planar symmetry this equation, in a slightly modified form, reads

$$\epsilon_r \epsilon_0 \frac{d^2 \phi}{dx^2} = - \sum_i z_i e C_{i0} \exp\{-(z_i e \phi + U_i)/kT\}. \quad [2]$$

In Eq. [2] ϵ_0 is the electric permittivity of vacuum, ϵ_r the relative permittivity, ϕ the electrostatic potential, C_{i0} the concentration of ion i at $\phi = 0$ and $z_i e$ its charge, k is the Boltzmann constant, and T the absolute temperature. U_i is an extra potential for ion i , and is normally not included in the PB equation. In the present case U_i is introduced to correct for the short-range interactions, giving rise to the ion specificity.

For a lamellar system (Fig. 1) the electric field is zero at the symmetry plane ($x = 0$), i.e.,



FIG. 1. Schematic representation of two parallel charged plates. The solid lines between the plates indicates the extra potentials U_i . r_Y and r_Z are the distances of closest approach for two competing counterions.

$$\left. \frac{d\phi}{dx} \right|_{x=0} = 0 \quad [3]$$

while at the lamellar surfaces ($x = \pm a$)

$$\left. \frac{d\phi}{dx} \right|_{x=\pm a} = \pm \frac{\sigma_s}{\epsilon_r \epsilon_0} \quad [4]$$

from Gauss's theorem. σ_s is the surface charge density. If the region $-a \leq x \leq a$ is considered homogenous, Eq. [2] has analytical solutions (6, 10).

In order to compare the experimental data with theoretical calculations, it is necessary to calculate the fraction of bound ions in a mixture of two types of ions, and check how this fraction varies with composition.

The square-well potential models. These models are schematically illustrated in Fig. 1. The magnitudes and extensions of the U_i 's in Eq. [2] are chosen in two distinct ways. The first way is to treat the extra potential as a hard-sphere potential using the appropriate ionic radii. This choice of potentials will divide the aqueous lamellae into three regions, one where no ions are present, the second where only the smaller ion is allowed, and a third region where both ions are present. An equivalent model has been proposed by Gregor and Gregor (11) for a cylindrical polyelectrolyte in discussing ion selectivity of ion exchange resins (12).

TABLE I
Parameters Used in the Calculations

Counterion	Ionic radius r (Å)	Potential energy U/kT	Equilibrium constant K (M^{-1})
Li	0.60	-1.0	0.1
Na	0.95	+1.0	0.025
K	1.33	+1.7	0.017
Cs	1.69	+1.0	0.025

The PB equation was solved for each region separately using an iterative procedure. The number of "bound" ions, to be compared with the experimental quadrupole splitting, was calculated from the final solution by integrating each ion concentration function a distance of 3 Å from the distances of closest approach. The choice of 3 Å is not crucial for the discussion of the variations in the amount of "bound" ions. In this model there is no adjustable parameter, in contrast to the other two models, where the calculated results are fitted to the experimental data.

The second way to use the square-well potentials is to assume a common region near the surface where each type of ion has an extra potential and is considered bound. The potentials can be either attractive or repulsive. The physicochemical interpretation of this model is not straightforward. Thus in the choice of the potentials and the extensions of them there is a great portion of arbitrariness. In this work the potentials were assumed to range 1 Å out from the lamellae, and the lithium potential was given a value of -1.0 (in units of kT). The fitting of the calculated results to the experimental data was made by a visual comparison.

The equilibrium constant model. The ion specificity can also be accounted for by allowing the ions to bind to the surface. The equilibrium constant for the binding of ion i to the surface is defined by

$$K_i = \frac{\alpha_i}{1 - \alpha} \frac{1}{C_i(a)} \quad (M^{-1}) \quad [5]$$

where α_i is the fraction of sites occupied

by i ions, α is the total fraction of bound ions, and $C_i(a)$ is the concentration of i ions at the lamellar surface. It is thus assumed that the electrostatic potential is equal at the binding site and at the surface. This model has been used when discussing site binding of monovalent cations to phospholipid vesicles (13, 14).

It is assumed that the ions bound to the surface are the only ones that give rise to the quadrupole splitting. In the present calculation the lithium equilibrium constant was given a value of $0.1 M^{-1}$, and the sodium and cesium constants were considered equal. The range of absolute values of the equilibrium constants, that will give reasonable fits to the experimental data, is about one order of magnitude.

In solving Eq. [2] with the various models the simplifying assumption was made that the amount of ionic amphiphile dissolved in the aqueous region is negligible. The thickness $2a$ of the water lamellae and the charge density σ , has been obtained by X-ray diffraction measurements (15), giving fixed values for the boundary conditions. In Table I the ionic radii, the square-well potentials, and the equilibrium constants used in the calculations are summarized. The computational techniques used are described in the Appendix.

RESULTS AND DISCUSSION

The system $C_7COONa-C_{10}OH-H_2O$ has been thoroughly investigated by Ekwall and co-workers (15) and the effect of changing the counterion has also received some attention. These studies show (16, 17) that the appearance of the phase diagram is rather independent of the particular choice of counterions, particularly at higher water contents. In the region of the lamellar phase where so-called one-dimensional swelling occurs, the counterion has a very small influence. It is in this region that NMR measurements indicate a single "bound" site.

At a few points (compositions are summarized in Table II) in this part of the lamel-

lar region ^7Li , ^{23}Na , and ^{131}Cs NMR quadrupole splittings were determined at varying proportions of the counterions Li^+ , Na^+ , K^+ , and Cs^+ . The results are summarized in Figs. 2a–f. Except for the cases (Na,Cs) and (K,Cs) the smaller ion has the highest affinity for binding and the observed splitting changes in an approximately linear way with composition. Figures 2a and c also demonstrate that an increase in the splitting of one ion is accompanied by a decrease for the other. It thus appears that the quadrupole splittings reflect a true competition in the counterion binding.

The solid lines in Figs. 2a–f are theoretical values calculated with the square-well model utilizing the ion sizes. With this model the affinity is always largest for the smaller ion. In general the calculated effects are too small. This finding is in sharp contrast to those obtained from models based on point charges, which always give too large calculated ion selectivities (2). One possibility is that the truth is somewhere in between and by assigning a constant charge density σ_s to the lamellar surface, the local nature of the ion binding has been underestimated. Of course there is also the possibility that other forces of short range are of importance. Particularly the results in (Na,Cs) and (K,Cs) systems indicate such a state of affairs.

The dashed lines in Figs. 2a–f represent the second potential model. The agreement with experiment is satisfactory, and from Table I it is seen that repulsive potentials also describe the ion specificity. It should be noted that there are more experimental curves than there are parameters to be determined. This is also the case for the equilibrium constant model, which is indicated by dotted lines in Figs. 2a–f. The equilibrium constants obtained by the fitting procedure are in comparable magnitude with those reported for alkali ion specificity to phospholipids (13,14). The magnitudes of the binding constants reveal that there are small effects involved in the

TABLE II
Experimental Details

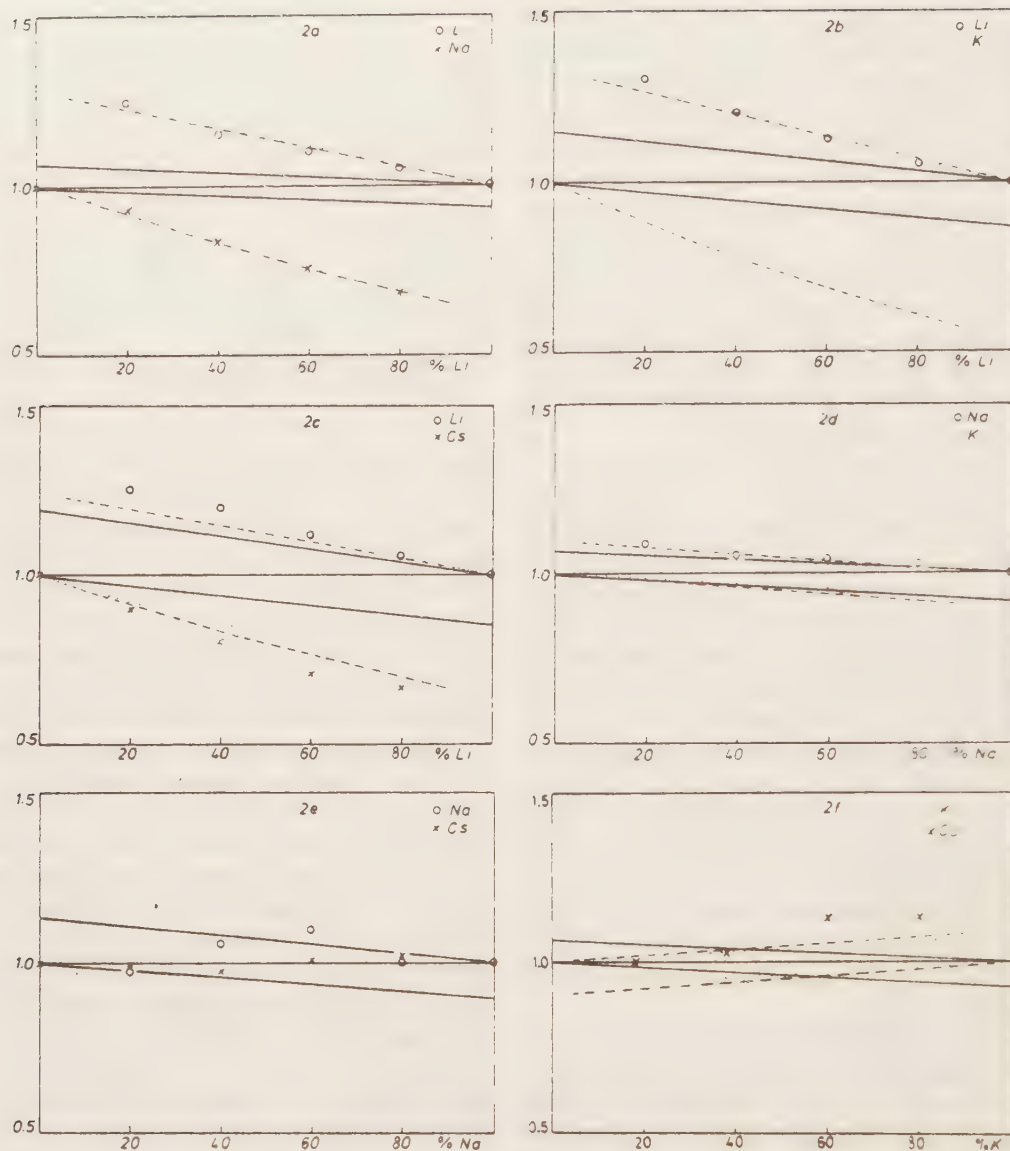
Relative molar composition $\text{C}_7\text{COO}^-:\text{D}_5\text{O}:\text{C}_{18}\text{OH}$	Counterions Y, Z	Splittings ^a (Hz)		Figure
		Δ_Y	Δ_Z	
1:59.7:2.73	Li, Na	444	7212	2a
1:59.2:2.75	Li, K	436	—	2b
1:29.8:2.60	Li, Cs	478	258	2c
1:59.2:2.74	Na, K	7215	—	2d
1:29.3:2.58	Na, Cs	5160	272	2e
1:29.6:2.57	K, Cs	—	267	2f

^a At 100% Y and Z, respectively.

site-binding. It should be noted that, since the extra potentials and equilibrium constants for Na and Cs are equal, no specificity lines will occur in Fig. 2e.

In the theoretical models no distinction can be made between the case where all the counterions remain hydrated or when they all lose one or more water in the first hydration shell in binding. For example, the addition of a water diameter to the ionic radii in the first potential model does not change the calculated specificity. It has the effect of moving the lamellas further apart, but will not influence the number of bound ions (6). However, it appears that the alkali cations have their first hydration sheath intact up to very low water contents (18). The observed quadrupole splitting is also more consistent with a hydrated ion (8). If a dehydration accompanies the binding of the counterions, it seems probable that the selectivity between the different ions will be greater.

On the other hand, the experimental results imply a selectivity sequence $\text{Li}^+ > \text{Na}^+, \text{Cs}^+ > \text{K}^+$ for the octanoate-decanol-water system. This sequence lies close to the so-called antilyotropic series ($\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$), but it does not correspond to any of the eleven most common series. According to Diamond and Wright (2), the obtained sequence indicates that the ions bind dehydrated to the lamellar surface, because, according to



FIGS. 2a-f. Experimental and theoretical quadrupolar splittings for two competing counterions as a function of their relative amounts. The concentration scale is in mole percent. Since the absolute magnitude of the splittings is irrelevant, these have been normalized by setting the splitting for 100% of one counterion equal to 1.0. (For absolute magnitudes see Table II). —, Ion size; ---, extra potential; ·····, equilibrium constant.

their terminology, the binding sites are strong. If the interaction between the surface site and the ion is strong compared to the hydration energy, dehydration occurs, and the antilyotropic series arises. If, on the other hand, the interaction is weak,

dehydration will at least not take place for the smaller alkali ions, and the reversed sequence will be favored. One can argue against the explanation above, by proposing, that if the interaction is weak enough, no dehydration will occur for any of

the alkali ions and the antilyotropic series will again show up.

It seems clear that the present methods or the point charge model used in (2) cannot give an adequate explanation to the transitions between the different affinity series. Polarizabilities, image charge effects, excluded volume effects etc. probably play important roles in the detailed interactions between the ions and the surface, and has to be dealt with by more elaborate methods, for instance Monte Carlo simulations.

SUMMARY

It has been demonstrated that the ion quadrupole splitting method is well suited for studying weak specific binding of alkali ions in lamellar liquid crystals. When the splittings from both types of ions were measured it gave an unambiguous indication of a true competitive behavior. The amphiphilic systems used have the great advantage of being thoroughly investigated. This makes the use of simple theoretical models to describe the specificity possible, since the structural parameters of the real systems are accurately known. It was shown that three such models, based on the Poisson-Boltzmann equation, could account for the observed ion specificity at least in a qualitative way. The affinity sequence obtained from the experiments does not belong to the most common ones, indicating that there are several different factors controlling the ion specificity.

APPENDIX

Computational Procedures

In the square-well potential models the extra potentials, i.e., the U_i 's, divide the aqueous lamellae into two different ion-containing regions, I and II (see Fig. 1). The PB equation in such a region R , for two different monovalent cations, Y and Z, reads

$$\epsilon_r \epsilon_0 \frac{d^2 \phi^R}{dx^2} = - \left\{ C_{Y0} \exp(-U_Y^R/kT) + C_{Z0} \exp(-U_Z^R/kT) \right\} \exp(-e\phi/kT). \quad [A1]$$

In the model where the ion sizes are taken into account, the values of U_i are

$$U_i = \begin{cases} 0, & 0 \leq x \leq a - r_i \\ \infty, & a - r_i \leq x \leq a \end{cases} \quad [A2]$$

where r_i is the ionic radius. Thus, in region II

$$C_{Z0} \exp(-U_Z/kT) \rightarrow 0,$$

$$\text{as } U_Z \rightarrow \infty. \quad [A3]$$

Equation [A1] has to be solved for each region separately, by assuming a certain fraction of the ion Y in region II, testing for continuity of the concentration of Y ions at $x = a - r_Z$, repeating this procedure until convergence is reached.

In the other potential model the U_i 's have finite values in region II, and in order to obtain a solution of Eq. [A1], the following conditions have to be fulfilled:

$$x_Y^I/x_Z^I = C_{Y0}/C_{Z0} \quad [A4]$$

$$x_Y^{II}/x_Z^{II} = (C_{Y0}/C_{Z0})$$

$$\times \exp\{-(U_Y^{II} - U_Z^{II})/kT\} \quad [A5]$$

$$x_Y^I + x_Y^{II} + x_Z^I + x_Z^{II} = 1. \quad [A6]$$

x_i^R is the fraction of ion i in region R . This problem was tackled by first solving the PB equation for the Y and Z ions separately. If one mixes the Y and Z ions, the fraction of ions in region II should be something in between the values from the separate solutions. If one chooses one such value, the electrostatic field is determined at $x = a - 1$ (Å) through Eq. [4], and it's possible to obtain C_{Y0} and C_{Z0} , and also the distribution of ions in the two regions via Eqs. [A4], [A5], and [A6].

In the equilibrium constant model the PB equation is first solved for the case of an unoccupied surface. The concentrations of the different ions at the surface are then put into Eq. [5], thus reducing the surface charge density. The PB equation is again solved with this new density and the procedure is repeated until both the PB equation and the equilibrium equations are satisfied.

e δ

The specificity is in all models defined as

$$\alpha_i(X_i) = \frac{n_{bi}(X_i)}{n_{bi}(X_i = 1)} \quad [A7]$$

where n_{bi} is the number of ions i that are considered bound, and X_i is the total fraction of the ion i .

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